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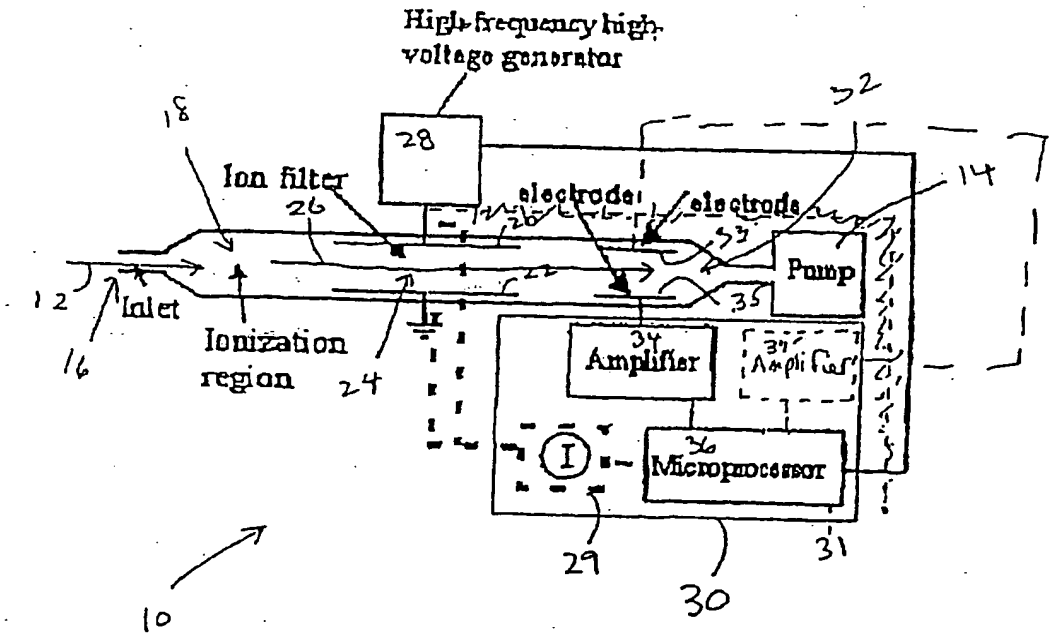
(54) Title: LONGITUDINAL FIELD DRIVEN FIELD ASYMMETRIC ION MOBILITY FILTER AND DETECTION SYSTEM



(57) Abstract: An asymmetric field ion mobility spectrometer (10) with ionization source (18) for ionizing a sample media and creating ions. An ion filter (24) is disposed in the analytical gap downstream from the ionization source for creating an asymmetric electric field to filter the ions. An ion flow generator for creating an electric field in a direction (26) transverse to the asymmetric electric field and which propels the ions through the asymmetric electric field towards a detector (32).

WO 01/35441 A1

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LONGITUDINAL FIELD DRIVEN FIELD ASYMMETRIC ION MOBILITY FILTER AND DETECTION SYSTEM

RELATED CASES

This application is a Continuation-In-Part Application of Application Serial No. 09/358,132 filed July 21, 1999.

FIELD OF INVENTION

This invention relates to a Longitudinal Field Driven Field Asymmetric Ion Mobility (FAIM) filter, and more particularly to a micromachined spectrometer.

BACKGROUND OF INVENTION

The ability to detect and identify explosives, drugs, chemical and biological agents as well as air quality has become increasingly more critical given increasing terrorist and military activities and environmental concerns. Previous detection of such agents was accomplished with conventional mass spectrometers, time of flight ion mobility spectrometers and conventionally machined FAIM spectrometers.

Mass spectrometers are very sensitive, highly selective and provide a fast response time. Mass spectrometers, however, are large and require significant amounts of power to operate. They also require a powerful vacuum pump to maintain a high vacuum in order to isolate the ions from neutral molecules and permit detection of the selected ions, and are also very expensive.

Another spectrometric technique which is less complex is time of flight

ion mobility spectrometry which is the method currently implemented in most portable chemical weapons and explosives detectors. The detection is based not solely on mass, but on charge and cross-section of the molecule as well. However, because of these different characteristics, molecular species identification is not as conclusive and accurate as the mass spectrometer. Time of flight ion mobility spectrometers typically have unacceptable resolution and sensitivity limitations when attempting to reduce their size, that is a drift tube length less than 2 inches. In time of flight ion mobility, the resolution is proportional to the length of the drift tube. The longer the tube the better the resolution, provided the drift tube is also wide enough to prevent all ions from being lost to the side walls due to diffusion. Thus, fundamentally, miniaturization of time of flight ion mobility systems leads to a degradation in system performance. While conventional time of flight devices are relatively inexpensive and reliable, they suffer from several limitations. First, the sample volume through the detector is small, so to increase spectrometer sensitivity either the detector electronics must have extremely high sensitivity, requiring expensive electronics, or a concentrator is required, adding to system complexity. In addition, a gate and gating electronics are usually needed to control the injection of ions into the drift tube.

FAIM spectrometry was developed in the former Soviet Union in the 1980's. FAIM spectrometry allows a selected ion to pass through a filter while blocking the passage of undesirable ions. One prior FAIM spectrometer was large and expensive, e.g., the entire device was nearly a cubic foot in size and cost over $25,000. These systems are not suitable for use in applications

requiring small detectors. They are also relatively slow, taking as much as one minute to produce a complete spectrum of the sample gas, are difficult to manufacture and are not mass producible.

Moreover, the pumps required to draw a sample medium into the spectrometer and to provide a carrier gas can be rather large and consume large amounts of power. And, the carrier gas necessarily must flow in the same direction as the ions which requires a structure which separates the analytical gap from the ionization source.

BRIEF SUMMARY OF THE INVENTION

It is therefore an object of this invention to provide a FAIM filter and detection system which can more quickly and accurately control the flow of selected ions to produce a sample spectrum than conventional FAIM devices.

It is a further object of this invention to provide such a filter and detection system which can detect multiple pre-selected ions without having to sweep the bias voltage.

It is a further object of this invention to provide such a filter and detection system which can even detect selected ions without a bias voltage.

It is a further object of this invention to provide such a filter and detection system which can detect ions spatially based on the ions' trajectories.

It is a further object of this invention to provide such a filter and detection system which has a very high resolution.

It is a further object of this invention to provide such a filter and detection system which can detect selected ions faster than conventional detection devices.

It is a further object of this invention to provide such a filter and detection system which has a sensitivity of parts per billion to parts per trillion.

It is a further object of this invention to provide such a filter and detection system which may be packaged in a single chip.

It is a further object of this invention to provide such a filter and detection system which is cost effective to implement and produce.

It is a further object of this invention to provide such a filter and detection system which does not require the high flow rate, high power consumption pumps normally associated with spectrometers.

This invention results from the realization that the pumps used to draw a sample media such as a gas into a FAIM spectrometer and to provide a flow of carrier gas can be made smaller or even eliminated in part by the incorporation of an ion flow generator which creates a longitudinal electric field in the direction of the intended ion travel path to propel the ions to the detector and through the transversely directed asymmetric electric field which acts as an ion filter.

The result is the ability to incorporate lower cost, lower flow rate, and smaller, even micromachined pumps; a decrease in power usage; the ability to now apply clean filtered gas (e.g., dehumidified air) in a direction opposite the direction of ion travel to eliminate ion clustering and the sensitivity of the spectrometer to humidity. Separate flow paths for the source gas and the clean filtered gas are no longer required thus reducing the structure required to maintain separate flow paths taught by the prior art. Moreover, if an electrospray nozzle is used as the ionization source, the electrodes used to create the fine droplets of solvent can be eliminated because the electrodes which create the longitudinal and transverse electric fields

function to both transport the ions and to create the fine spray of solvent droplets.

The spectrometer can be made extremely small, if required, and used in chemical and military applications, as a filter for a mass spectrometer, as a detector for a gas chromatograph, as a front end to a time of flight ion mobility spectrometer for increased resolution or as a filter for a flexural plate wave device.

The invention results from the further realization that an extremely small, accurate and fast FAIM filter and detection system can be achieved by defining a flow path between a sample inlet and an outlet using a pair of spaced substrates and disposing an ion filter within the flow path, the filter including a pair of spaced electrodes, one electrode associated with each substrate and a controller for selectively applying a bias voltage and an asymmetric periodic voltage across the electrodes to control the path of ions through the filter.

The invention results from the further realization that by providing an array of filters, each filter associated with a different bias voltage, the filter may be used to detect multiple selected ions without sweeping the bias voltage.

The invention results from the further realization that by varying the duty cycle of the periodic voltage, no bias voltage is required.

The invention results from the further realization that by segmenting the detector, ion detection may be achieved with greater accuracy and resolution by detecting ions spatially according to the ions' trajectories as the ions exit the filter.

This invention features an ion mobility spectrometer comprising an ionization source for ionizing a sample media and creating ions; an analytical gap; an ion filter disposed in the analytical gap downstream from the ionization source for creating an asymmetric electric field to filter the ions; an ion flow generator for

creating an electric field in a direction transverse to the asymmetric electric field which is in the longitudinal direction for propelling ions through the asymmetric electric field; and an ion detector for sensing ions not filtered by the ion filter.

The ion detector is typically located proximate to the ion flow generator. The spectrometer may be a radiation source, an ultraviolet lamp, a corona discharge device, or an electrospray nozzle.

The ion filter is preferably connected to an electric controller for applying a bias voltage and an asymmetric periodic voltage to the ion filter. The ion filter typically includes a pair of spaced electrodes for creating an asymmetric electric field between them. The ion flow generator typically includes a plurality of spaced discrete electrodes insulated from these electrodes for creating the transverse direction electric field which propels the ions through the asymmetric electric field and to the detector.

Alternatively, the ion flow generator includes spaced resistive layers and a voltage is applied along each layer to create the longitudinally directed electric field which propels the ions through the asymmetric electric field and to the detector.

In another embodiment, the ion filter includes a first plurality of discrete electrodes electrically connected to an electric controller which applies an asymmetric periodic voltage to them. The ion flow generator includes a second plurality of discrete electrodes dispersed among the electrodes of the ion filter and connected to a voltage source which applies a potential gradient along the second plurality of discrete electrodes.

The analytical gap typically is enclosed by a housing. The ion filter

includes electrodes on an inside surface of the housing and the ion flow generator includes electrodes proximate but insulated with respect to the ion filter electrodes. The ion detector also includes electrodes on an inside surface of the housing proximate to the ion filter and the ion flow generator.

The analytical gap is typically enclosed by a housing, the ion filter may include electrodes on an outside surface of the housing and the ion flow generator then includes resistive layers on an inside surface of the housing. A voltage is applied along each resistive layer to create a longitudinal electric field. Alternatively, the ion filter and the ion flow generator are combined and include a series of discrete conductive elements each excited by a voltage source at a different phase.

BRIEF DESCRIPTION OF THE DRAWINGS

Other objects, features and advantages will occur to those skilled in the art from the following description of a preferred embodiment and the accompanying drawings, in which:

Fig. 1 is a schematic block diagram of the micromachined filter and detection system according to the present invention;

Fig. 2 is a schematic representation of the ions as they pass through the filter electrodes of Fig. 1 toward the detector;

Fig. 3A is a graphical representation of the bias voltage required to detect acetone and the sensitivity obtainable;

Fig. 3B is a representation, similar to Fig. 3A, of the bias voltage required to detect Diethyl methyl amine;

Fig. 4 is a cross sectional view of the spaced, micromachined filter according to the present invention;

Fig. 5 is a three dimensional view of the packaged micromachined filter and detection system, including fluid flow pumps, demonstrating the miniaturized size which may be realized;

Fig. 6 is an exploded view of one embodiment according to the present invention in which an array of filters and detectors are disposed in the same flow path;

Fig. 7 is an exploded view, similar to Fig. 6, in which the array of filters is stacked and one filter and detector is associated with a single flow path.

Fig. 8 is a cross sectional representation of a single flow path of the arrayed filter and detector system of Fig. 7;

Fig. 9 is graphical representation demonstrating identification of individual chemicals from a mixture of benzene and acetone;

Fig. 10 is a schematic block diagram, similar to Fig. 1, in which the filter is not compensated by a bias voltage and the duty cycle of the periodic voltage is instead varied to control the flow of ions through the filter;

Fig. 11 is a graphical representation of an asymmetric periodic voltage having a varying duty cycle which is applied to the filter of Fig. 9 to filter selected ions without a bias voltage;

Fig. 12 is a schematic diagram of a filter and detector system in which the detector is segmented to spatially detect ions as they exit the filter;

Fig. 13 is a schematic view of a typical prior art spectrometer;

Fig. 14 is a schematic view of one embodiment of the longitudinal field

driven ion mobility spectrometer of the subject invention;

Fig. 15 is a schematic view of another embodiment of the longitudinal field driven ion mobility spectrometer of this invention;

Fig. 16 is a schematic view of another embodiment of the longitudinal field driven ion mobility spectrometer of this invention;

Fig. 17 is a schematic view of the ion filter, detector, and ion flow generator portion of the spectrometer of this invention;

Fig. 18 is a schematic view of another embodiment of the ion filter, detector, and ion flow generator portion of a spectrometer according to this invention;

Fig. 19 is a schematic view of another embodiment of the ion filter, detector, and ion flow generator portion of a spectrometer according to this invention;

Figs. 20 is a schematic view of another embodiment of the ion filter, detector, and ion flow generator portion of a spectrometer according to this invention; and

Fig. 21 is a schematic view of another embodiment of the ion filter, detector, and ion flow generator portion of a spectrometer according to this invention.

PREFERRED EMBODIMENT

FAIM spectrometer 10, Fig. 1, operates by drawing a gas, indicated by arrow 12, via pump 14, through inlet 16 into ionization region 18. The ionized

gas is passed between parallel electrode plates 20 and 22, which comprise ion filter 24, following flow path 26. As the gas ions pass between plates 20 and 22, they are exposed to an electric field between electrode plates 20 and 22 induced by a voltage applied to the plates by voltage generator 28 in response to electronic controller 30. The electric field produced preferably is asymmetric and oscillates in time.

As ions pass through filter 24, some are neutralized by plates 20 and 22 while others pass through and are sensed by detector 32. Detector 32 includes a top electrode 33 at a predetermined voltage and a bottom electrode 35, typically at ground. Top electrode 33 deflects ions downward to electrode 35. However, either electrode may detect ions depending on the ion and the voltage applied to the electrodes. Moreover, multiple ions may be detected by using top electrode 33 as one detector and bottom electrode 35 as a second detector. Electronic controller 30 may include, for example, amplifier 34 and microprocessor 36. Amplifier 34 amplifies the output of detector 32, which is a function of the charge collected by electrode 35 and provides the output to microprocessor 36 for analysis. Similarly, amplifier 34', shown in phantom, may be provided where electrode 33 is also utilized as a detector.

As ions 38, Fig. 2, pass through alternating asymmetric electric field 40, which is transverse to gas flow 12, electric field 40 causes the ions to "wiggle" along paths 42a, 42b and 42c. Time varying voltage V is typically in the range of ± (1000-2000) volts and creates electric field 40 with a maximum field strength of 40,000 V/cm. The path taken by a particular ion is a function of its mass, size, cross-section and charge. Once an ion reaches electrode 20 or 22, it is

neutralized. A second, bias or compensation field 44, typically in the range of ± 2000 V/cm due to a ± 100 volt dc voltage, is concurrently induced between electrodes 20 and 22 by a bias voltage applied to plates 20 and 22, also by voltage generator 28, Fig. 1, in response to microprocessor 36 to enable a preselected ion species to pass through filter 24 to detector 32. Compensation field 44 is a constant bias which offsets alternating asymmetric field 40 to allow the preselected ions, such as ion 38c to pass to detector 32. Thus, with the proper bias voltage, a particular species of ion will follow path 42c while undesirable ions will follow paths 42a and 42b to be neutralized as they encounter electrode plates 20 and 22.

The output of FAIM spectrometer 10 is a measure of the amount of charge on detector 32 for a given bias electric field 44. The longer the filter 24 is set at a given compensation bias voltage, the more charge will accumulate on detector 32. However, by sweeping compensation voltage 44 over a predetermined voltage range, a complete spectrum for sample gas 12 can be achieved. The FAIM spectrometer according to the present invention requires typically less than thirty seconds and as little as one second to produce a complete spectrum for a given gas sample.

By varying compensation bias voltage 44 the species to be detected can be varied to provide a complete spectrum of the gas sample. For example, with a bias voltage of

-3.5 volts acetone was detected as demonstrated by concentration peaks 46, Fig. 3A in concentrations as low as 83 parts per billion. In contrast, at a bias voltage of -6.5 volts, diethyl methyl amine, peaks 48, Fig. 3B, was detected in

concentrations as low as 280 parts per billion.

Filter 24, Fig. 4, is on the order of one inch in size. Spectrometer 10 includes spaced substrates 52 and 54, for example glass such as Pyrex® available from Corning Glass, Corning, N.Y., and electrodes 20 and 22, which may be for example gold, titanium, or platinum, mounted or formed on substrates 52 and 54, respectively. Substrates 52 and 54 are separated by spacers 56a and 56b which may be formed by etching or dicing silicon wafer. The thickness of spacers 56a-b defines the distance between electrodes 20 and 22. Moreover, applying the same voltage to silicon spacers 56a-b, typically ± (10-1000 volts dc) transforms spacers 56a and 56b into electrodes which can produce a confining electric field 58, which guides or confines the ions' paths to the center of flow path 26, Fig. 1, in order to obtain a better sample spectrum. To confine the ions, spacer electrodes 56a-b must be set to the appropriate voltages so as to "push" the ions to the center of flow path 26. This increases the sensitivity of the system by preserving more ions so that more ions strike electrodes 33 and 35. However, this is not a necessary limitation of the invention.

To maintain accurate and reliable operation of spectrometer 10, neutralized ions which accumulate on electrode plates 20 and 22 must be purged. This may be accomplished by heating flow path 26. For example, controller 30, Fig. 1, may include current source 29, shown in phantom, which provides, in response to microprocessor 36, a current I to electrode plates 20 and 22 to heat the plates, removing accumulated molecules. Similarly, current I may instead be applied to spacer electrodes 56a and 56 b, Fig. 4, to heat flow path 26 and clean plates 20 and 22.

Packaged FAIM spectrometer 10, Fig. 5, may be reduced in size to one inch by one inch by one inch. Pump 14 is mounted on substrate 52 for drawing a gas sample 12 into inlet 16. Clean dry air may be introduced into flow path 26, Fig. 1, by recirculation pump 14a prior to or after ionization of the gas sample. Electronic controller 30 may be etched into silicon control layer 60 which combines with substrates 52 and 54 to form a housing for spectrometer 10. Substrates 52 and 54 and control layer 60 may be bonded together, for example, using anodic bonding, to provide an extremely small FAIM spectrometer. Micro pumps 14 and 14a provide a high volume throughput which further expedites the analysis of gas sample 12. Pumps 14 and 14a may be, for example, conventional miniature disk drive motors fitted with small centrifugal air compressor rotors or micromachined pumps, which produce flow rates of 1 to 4 liters per minute. One example of pump 14 is available from Sensidyne, Inc., Clearwater, Florida.

While the FAIM spectrometer according to the present invention quickly produces a spectrum for a particular gas sample, the time for doing so may be further reduced with an array of filters 32. FAIM spectrometer 10, Fig. 6, may include filter array 62, a single inlet 16 and single flow path 26. Sample gas 12 is guided by confining electrodes 56a-h to filter array 62 after passing by ionization source 18, which may include an ultraviolet light source, a radioactive device or corona discharge device. Filter array 62 includes, for example, paired filter electrodes 20a-e and 22a-e and may simultaneously detect different ion species by applying a different compensation bias field 44, Fig. 2, to each electrode pair and sweeping each electrode pair over a different voltage range greatly reducing the sweep time. However, array 62 may include any number of filters depending

on the size of the spectrometer. Detector array 64, which includes detectors 32a-e, detects multiple selected ion species simultaneously, thereby reducing the time necessary to obtain a spectrum of the gas sample 12. The electrode pairs share the same asymmetric periodic ac voltage 40.

Clean dry air may be introduced into flow path 26 through clean air inlet 66 via recirculator pump 14a, Fig. 5. Drawing in clean dry air assists in reducing the FAIM spectrometer's sensitivity to humidity. Moreover, if the spectrometer is operated without clean dry air and a known gas sample is introduced into the device, the device can be used as a humidity sensor since the resulting spectrum will change with moisture concentration from the standardized spectrum for the given sample.

However, rather than each filter 32a-e of filter array 62 sharing the same flow path 26, individual flow paths 26a-e, Fig. 7, may be provided so that each flow path has associated with it, for example, inlet 16a , ionization region 18a, confining electrodes 56a', 56b', ion filter electrode pair 20a, 22a, detector electrode pair 33a, 35a and exit port 68a.

In operation, sample gas 12 enters sample inlet 16a, Fig. 8, and is ionized by, for example, a corona discharge device 18a. The ionized sample is guided towards ion filter 24a by confining electrodes 56a and 56b. As ions pass between ion filter electrodes 20a and 22a, undesirable ions will be neutralized while selected ions will pass through filter 24a to be detected by detector 32a.

As shown in Fig. 9, identification of individual constituents of a mixture is demonstrated by the distinct Benzene peaks 50 and the acetone peaks 51.

It has also been found that a compensation bias voltage is not necessary to

detect a selected specie or species of ion. By varying the duty cycle of the asymmetric periodic voltage applied to electrodes 20 and 22 of filter 24, Fig. 10, there is no need to apply a constant bias voltage to plate electrodes 20 and 22. Voltage generator 28, in response to control electronics 30 varies the duty cycle of asymmetric alternating electric field 40. By varying the duty cycle of periodic electric field 40, Fig. 11, the path of selected ion 32c may be controlled. As an example, rather than a limitation, the duty cycle of field 40 may be one quarter: 25% high, peak 70, and 75% low, valley 72, and ion 38c approaches plate 20 to be neutralized. However, by varying the duty cycle of voltage 40a to 40%, peak 70a, ion 38c passes through plates 20 and 22 without being neutralized. Typically the duty cycle is variable from 10-50% high and 90-50% low. Accordingly, by varying the duty cycle of field 40, an ion's path may be controlled without the need of a bias voltage.

To improve FAIM spectrometry resolution even further, detector 32, Fig. 12, may be segmented. Thus, as ions pass through filter 24 between filter electrodes 20 and 22, the individual ions 38c'-38c'''' may be detected spatially, the ions having their trajectories 42c'-42c'''' determined according to their size, charge and cross section. Thus detector segment 32' will have a concentration of one species of ion while detector segment 32'' will have a different ion species concentration, increasing the spectrum resolution as each segment may detect a particular ion species.

One prior art ion mobility spectrometer 200, Fig. 13, (See U.S. Patent No. 5,420,424) includes analytical gap 202 defined by the space between inner 204 and outer 206 longitudinal electrodes. Sample media, or a source gas is drawn

through inlet 210 via the action of pump 212 and ionized by ionization source 214. A carrier gas is introduced via pump 216 into analytical gap 202. Ions generated by ionization source 214 travel through aperture 218 by the action of electrode 220 and into analytical gap 202 until they reach detector 224.

Such a structure requires two pumps 212 and 216, and separate flow paths 201 and 203 for the source gas and the carrier gas. Thus, prior art mobility spectrometer 200 cannot be made very small, and requires sufficient power to operate pumps 212 and 216.

In the subject invention, the need for pumps 212 and 216 is either eliminated or the pumps are made smaller, even micromachined pumps can be used, for example. Furthermore, separate flow paths for the source gas and the carrier gas are not required and clean filtered gas such as dehumidified air can be introduced to flow in a direction opposite the direction of ion travel to eliminate ion clustering and to improve (lower) the spectrometer's sensitivity to the effects of humidity.

Field asymmetric ion mobility spectrometer 230 according to this invention, Fig. 14, includes analytical gap 232 inside structure 234 which may be a round tube or a small flat housing with walls defining an enclosure. Ionization source 236 ionizes a sample media or gas driven into analytical gap 232 via the action of pump 238 which may be a micromachined pump with a flow rate of much less than the typically required 1-4 liters per minute of the prior art resulting in a power savings of between 1-5 watts over prior art spectrometers.

Ion filter 240 is disposed in analytical gap 232 downstream from ionization source 236 for creating an asymmetric electric field shown by vector

242 to filter ions generated by ionization source 236 as discussed *supra*.

Ion filter 240 typically includes a pair of spaced electrodes 248 and 246 connected to an electric controller which applies a biased voltage and an asymmetric periodic voltage to electrodes 246 and 248, see Figs. 1-2.

Unique to spectrometer 230 is ion flow generator 250 for creating a longitudinal electric field as shown by vector 252. The strength of longitudinal and electric field 252 can be constant in time or space or can vary with time and space and propels ions through asymmetric electric field 242.

In one embodiment, ion flow generator 250 includes discrete electrodes 260, 262, 264, and 266 insulated from electrode 246 and discrete electrodes 248 by insulating mediums 268. In one example, electrode 260 is at 1,000 volts, electrode 266 is at 10 volts and electrodes 262 and 264 are at 500 and 100 volts respectively, although these voltage levels may vary depending on the specific implementation of spectrometer 230. The voltages applied to electrodes 261, 263, 265, and 267 generally match the voltages applied to electrodes 260, 262, 264, and 266, respectively. There may be more or fewer electrodes opposing each other forming ion flow generator 250. Electrode pairs (260, 261), (262, 263), (264, 265), and (266, 267) can also each be a ring electrode as well as discrete planar electrodes.

In any case, the strength of longitudinal electric field 252 propels ions generated by ionization source 236 through asymmetric electric field 242 and towards detector 270 thus eliminating or reducing the flow rate and power requirements of pumps 212 and 216, Fig. 13 of the prior art.

Typically, detector 270 is positioned close to ion flow generator 250 and

electrodes 260, 262, 264, 266, 261, 263, 265, and 267 preferably occupy more or less the same physical space as ion filter 240 electrodes 246 and 248 relative to analytical gap 232.

In another embodiment, spectrometer 300, Fig. 15, includes structure which defines flow path 302 and analytical gap 304 with an opening 306 there between. Source gas is drawn into flow path 302 by pump 310 and ionized by ionization source 308. The ions are deflected through opening 306 and into analytical gap 304 by deflecting electrodes 312 and 313 where the electrodes of ion flow generator 250 and ion filter 240 are disposed. Ion flow generator 250 propels the ions through the asymmetric ion field created by filter 240 as discussed above. In this way, pump 312 need only supply a fairly low flow rate of dehumidified air into analytical gap 304 and no carrier gas flow is required as taught by the prior art.

In another embodiment, a desiccant 322, Fig. 16, is provided in housing 320 and small pump 324 is the only pump required to draw source gas into housing 320 through small orifice 326. Ionization source 328 produces ions which travel through filter 240 aided by the longitudinal electric field created by ion flow generator 250 positioned proximate detector 330.

In one embodiment detector 270, Fig. 14, includes spaced electrodes 272, 274, Fig. 17, similar in construction to electrodes 33 and 35, Fig. 1. The ion filter of Fig. 17 includes spaced electrodes 276 and 278 for creating transverse electric field 280. The ion flow generator includes spaced discrete electrodes as shown for electrodes 282 and 284 and electrodes 286 and 288. Electrodes 282 and 284 may be at 1000 volts and electrodes 286 and 288 may be at 0 volts.. Insulating

medium 290 and 292 insulates electrodes 282, 284, 286, and 288 with respect to electrodes 276 and 278. Electrode pairs (282, 284) through (286, 288) or more could also be ring electrodes.

In another embodiment, Fig. 18, the ion filter includes spaced resistive layers 300 and 302 insulated from electrodes 276 and 278 on Pyrex substrate 310 by insulating medium 290 and 292, for example, a low temperature oxide material.

Resistive layers 300 and 302 may be a resistive ceramic material deposited on insulating layers 290 and 292, respectively. Terminal electrodes 312, 314, 316 and 318 make contact with each resistive layer to apply a voltage drop across each resistive layer to generate the longitudinal electric field. Thus, electrodes 312 and 316 may be at 1000 volts while electrodes 314 and 318 may be at 0 volts. This embodiment can be extended to a cylindrical geometry by making electrodes 312 and 316 a ring electrode, electrodes 314 and 318 a ring electrode, and resistive layers 300 and 302 an open cylinder.

In still another embodiment, Fig. 19, the ion filter includes a plurality of high frequency, high voltage electrodes 330, 332, 334 and 336 connected to an electric controller (see Fig. 1) which applies an asymmetric periodic voltage to create an ion filtering electric field and the ion flow generator includes a second plurality of discrete electrodes 338, 340, 342 and 344 dispersed among but insulated from the discrete electrodes of the ion filter as shown and connected to a voltage source which applies a potential gradient across them to generate an ion propelling electric field which is in directed in a direction transverse to the ion filtering electric field.

In still another embodiment, Fig. 20, high frequency electrodes 350, 352 which provide the asymmetric ion filtering electric field are disposed on the outside of walls 354 and 356 made of an insulative material such as PYREX which define analytical gap 358. Resistive layers 360 and 362 may be a resistive ceramic material deposited on the inside of walls insulating walls 354 and 356, respectively. Terminal electrodes 364 and 366, and 368 and 370 make contact with each resistive layer is shown to apply a voltage drop across each resistive layer to generate the ion propelling longitudinal electric field. Thus, electrodes 364 and 368 may each be at 1000 volts while electrodes 366 and 370 are at 0 volts.

In the design shown in Fig. 21, discrete electrodes 380-386 and 387-394 produce an electrical field with both transverse and longitudinal components to both filter and propel the ions. A travelling wave voltage of the form

$$V\cos(wt-kz) \quad (1)$$

where $k = 2\pi/\lambda$ is the wave number has an associated electric field with both transverse and longitudinal components. For a planar system, each succeeding set of opposing electrodes is excited by a voltage source at a fixed phase difference from the voltage source applied to the adjacent set of opposing electrodes.

Thus, electrodes 380 and 387 are excited with a voltage of vcos(wt) while electrodes 381 and 388 are excited with a voltage of vcos (wt + 120) and so on as shown in Fig. 21. Travelling wave voltages require polyphase voltage excitations, the simplest being a two phase excitation. So, a two conductor ribbon could also be wound around a duct defining the analytical gap with one

conductor excited at vcos (wt) and the other conductor excited at vsin (wt). Three phase excitations could be incorporated if the conductor ribbon or tape had three conductors.

The subject designs lend themselves well to the use of an electrospray ionization source nozzle because certain electrodes can function both as the source for the longitudinal electrical field which transports the ions towards the detector electrodes and as the electrodes which create a fine spray of solvent droplets for ionizing the source gas or sample medium.

Thus, in accordance with this invention, pumps 216 and 212, Fig. 13 of the prior art are either eliminated or at least reduced in size and have lower flow rate and power requirements. By the incorporation of an ion flow generator which creates a longitudinal electric field in the direction of the intended ion travel, the ions are propelled to the detector and through the transversely directed asymmetric electric field which acts as an ion filter. In the preferred embodiment, a pump is not required to draw the ionized gas species through the spectrometer drift tube for analysis. Instead, a longitudinal electric field applied along the length of the drift tube can be used to propel the ions down the drift tube through the ion filter to a detector. By eliminating the high flow rate (1-4 liters per minute) pumps used in prior art spectrometers, a significant reduction in power consumption, size, and cost can be realized leading to a truly miniaturized spectrometer on a chip.

A second benefit of this design is that a flow of clean filtered air can be applied in a direction opposite the direction of the motion of the ions. In this way, any neutrals in the sample gas which were not ionized are deflected away

and do not enter the ion analysis region. The result is the elimination of ion clustering problems and the humidity sensitivity of the sensor. Because the flow rates are low, it is possible to incorporate integrated micromachine pumps.

Since only the ions need enter the analysis region, no gas flow is required in the ion filter and detector region. Molecular sieves can be located close to the entrance of this region in order to absorb any neutral molecules in the analysis region and prevent clustering. A separate source of air flow delivered by a pump in the ion filter (analyzer) region is not required in contrast to the prior art which incorporated high flow rate pumps which consumed a relatively large amount of power (1-5 watts) and which added size to the system and/or which could fail. In subject invention, a flow of neutral gas in the same direction as the ion species generated from the sample gas to be analyzed is not required. Instead a flow gas in the opposite direction of the ion flow direction can be applied to keep the ion filter region free of unwanted neutrals and moisture. A higher gas flow rate through the ion filter (drift tube) is not required. Instead, the ions are drawn through the ion filter (drift tube) along the z axis by a longitudinal electric field produced by a small potential gradient in the z direction. In the design shown, Fig. 17, only a low volume flow in the direction of the longitudinal electric field as shown by vector 252 is required to bring the ions proximate to electrodes 282 and 284. No gas flow is required in the ion filter and detector region due to longitudinal electric field 252. Also, if required, a low flow volume of clean filtered air can be provided in a direction opposite the longitudinal electric field to keep the ion filter and detector region free of neutrals. A resistive divider circuit provides a potential gradient across electrodes 282, 284, so that for example,

electrodes 282 and 284 are at 1000 volts while electrodes 286 and 288 are at 0 volts. In the design shown in Fig. 19, all the high frequency electrodes 330, 332, etc. are electrically tied together while the longitudinal field producing electrodes 338, 340 etc. have a potential gradient dropped across them. In one embodiment, the voltages applied to the electrodes can be alternated so that first a voltage is applied to generate the transverse electric field and then a voltage is applied to other electrodes to generate the longitudinal electric field.

Although specific features of the invention are shown in some drawings and not in others, this is for convenience only as each feature may be combined with any or all of the other features in accordance with the invention.

Other embodiments will occur to those skilled in the art and are within the following claims:

What is claimed is:

CLAIMS

1. An asymmetric field ion mobility spectrometer comprising:

an ionization source for ionizing a sample media and creating ions;

an analytical gap;

an ion filter disposed in the analytical gap downstream from the ionization source for creating an asymmetric electric field to filter the ions;

an ion flow generator for creating an electric field transverse to the asymmetric electric field for propelling ions through the asymmetric electric field; and

an ion detector for sensing ions not filtered by the ion filter.

2. The spectrometer of claim 1 in which the ion detector is proximate the ion flow generator.

3. The spectrometer of claim 2 in which the ionization source is a radiation source.

4. The spectrometer of claim 1 in which the ionization source includes an ultraviolet lamp.

5. The spectrometer of claim 1 in which the ionization source includes a corona discharge device.

6. The spectrometer of claim 1 in which the ionization source includes an electrospray nozzle.

7. The spectrometer of claim 1 in which the ion filter is connected to an electric controller for applying a bias voltage and an asymmetric periodic voltage to the ion filter.

8. The spectrometer of claim 1 in which the ion filter includes a pair of spaced electrodes for creating an asymmetric electric field and the ion flow generator includes a plurality of spaced discrete electrodes insulated from the pair of spaced electrodes for creating the transverse direction varying strength electric field.

9. The spectrometer of claim 1 in which the ion flow generator includes spaced resistive layers and a voltage applied along each layer to create a longitudinal electric field.

10. The spectrometer of claim 1 in which the ion filter includes a first plurality of discrete electrodes electrically connected to an electric controller which applies an asymmetric periodic voltage to the first plurality of discrete electrodes and in which the ion flow generator includes a second plurality of discrete electrodes dispersed among the first plurality of discrete electrodes connected to a voltage source which applies a potential gradient along the second plurality of discrete electrodes.

11. The spectrometer of claim 1 in which the analytical gap is enclosed by a housing, the ion filter includes electrodes on an inside surface of the housing and the ion flow generator includes electrodes proximate but insulated with respect to the ion filter electrodes.

12. The spectrometer of claim 11 in which the ion detector includes electrodes on an inside surface of the housing proximate the ion filter and the ion flow generator.

13. The spectrometer of claim 1 in which the analytical gap is enclosed by a housing, the ion filter includes electrodes on an outside surface of the housing and the ion flow generator includes resistive layers on an inside surface of the housing and a voltage is applied along each layer to create a longitudinal electric field.

14. The spectrometric of claim 1 in which the ion filter and the ion flow generator are combined and include a series of discrete conductive elements each excited by a voltage source at a different phase.

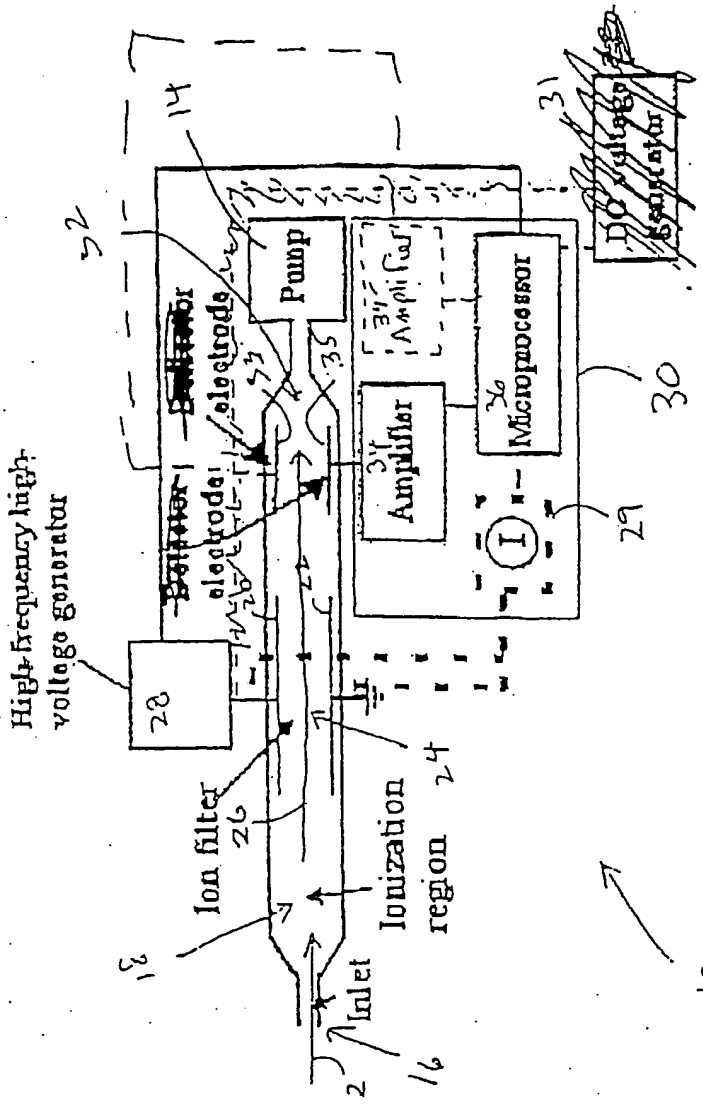
High-frequency high-voltage generator
28
Ion filter
26
Ionization region
24
Inlet
16
12
18
10
Pump
electrode
Amplifier
Microprocessor
30
29
31
32
35

Fig. 1

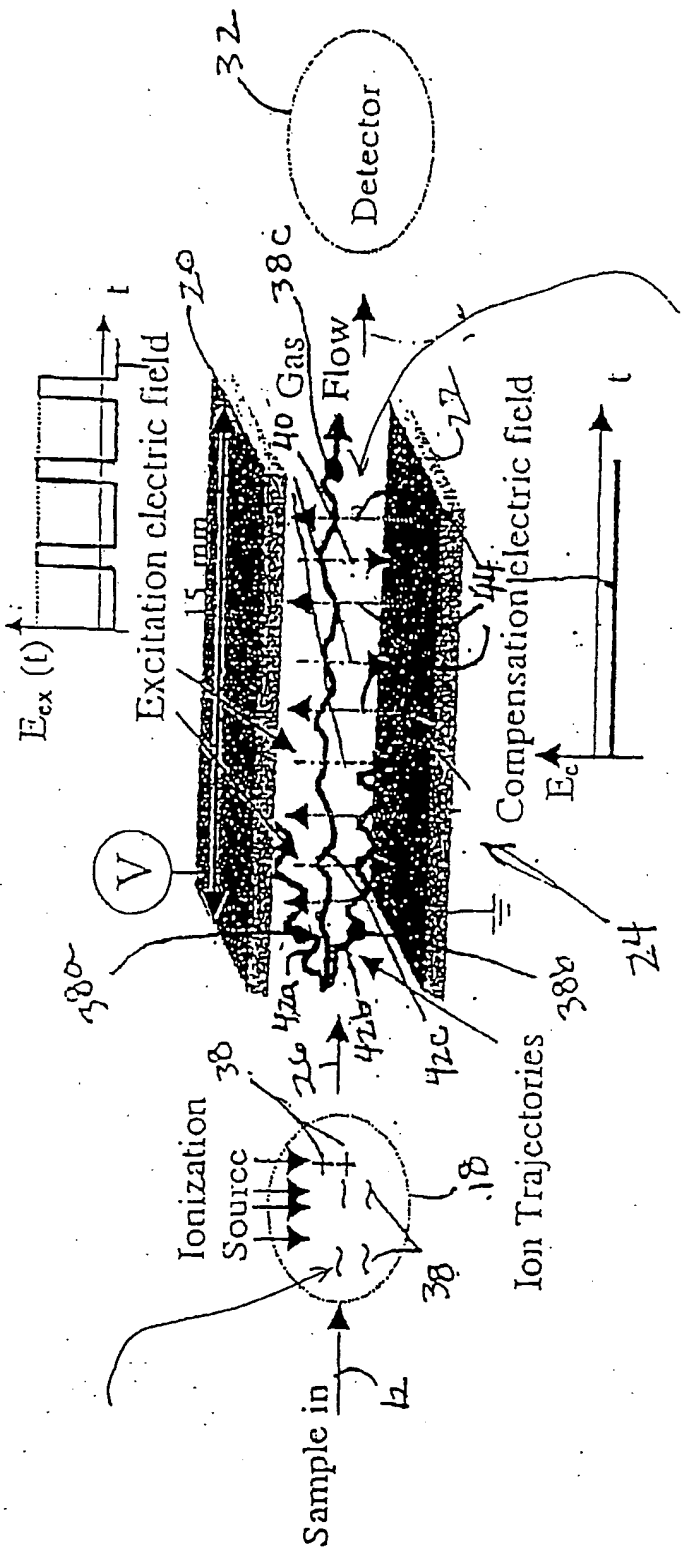
Detector
Flow
Gas
Excitation electric field
Compensation electric field
Ionization Source
Ion Trajectories
Sample in
V
t
15 mm

FIG. 2

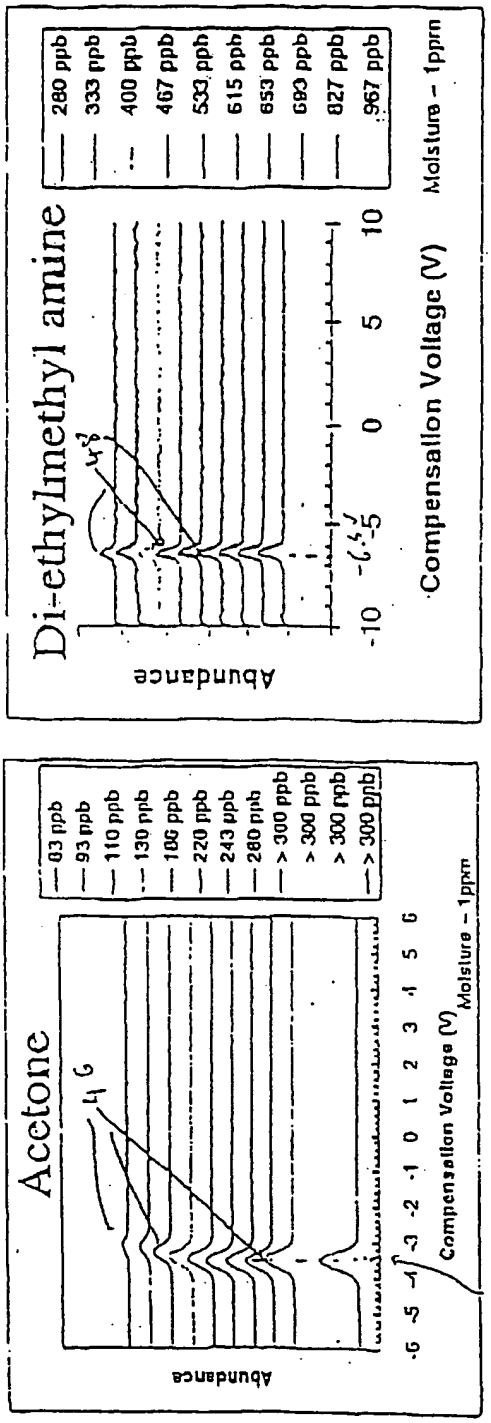

Fig. 3a: Response of FAIMS to varying concentrations of Acetone and Di-ethylmethyl amine

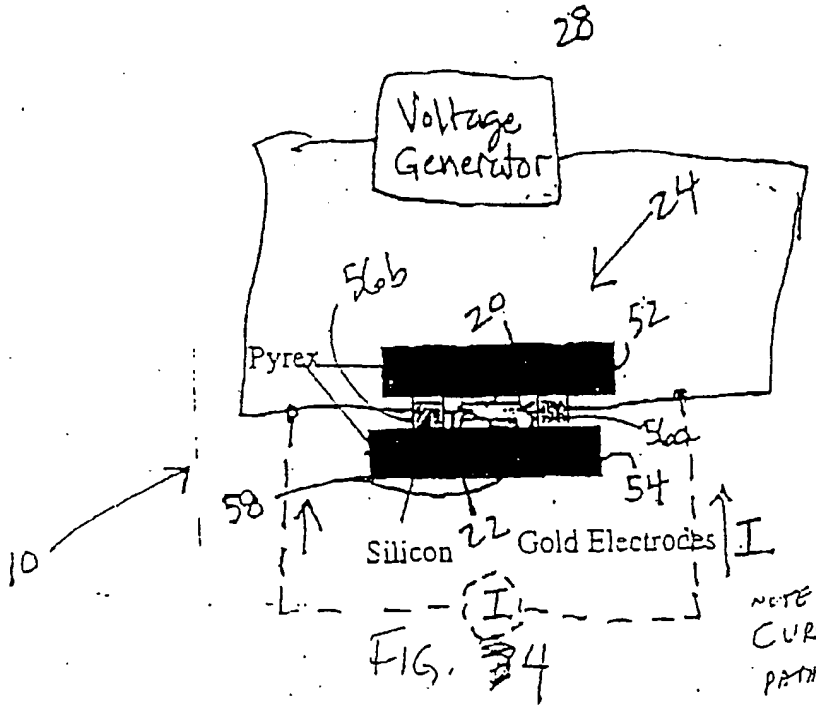
28
Voltage Generator
24
56b
20
52
Pyrex
56a
54
58
Silicon
22
Gold Electrodes
I
10
NOTE! CURRENT RETURN PATHS NOT SHOWN

FIG. 4

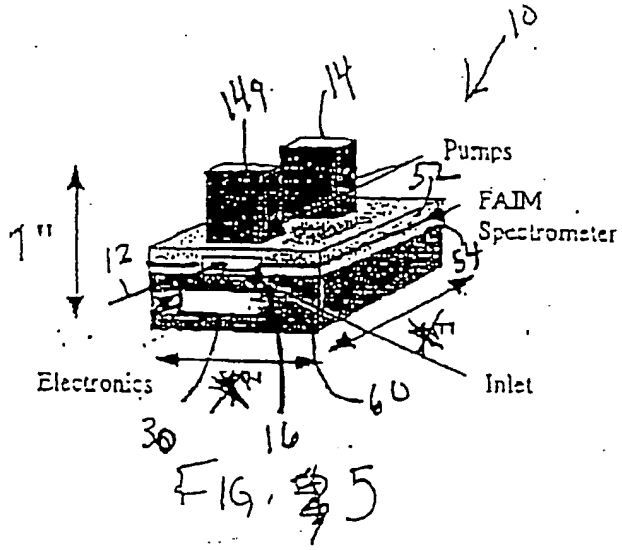
10
14a
14
Pumps
56
FAIM
Spectrometer
54
1"
12
Electronics
60
Inlet
30
16

FIG. 5

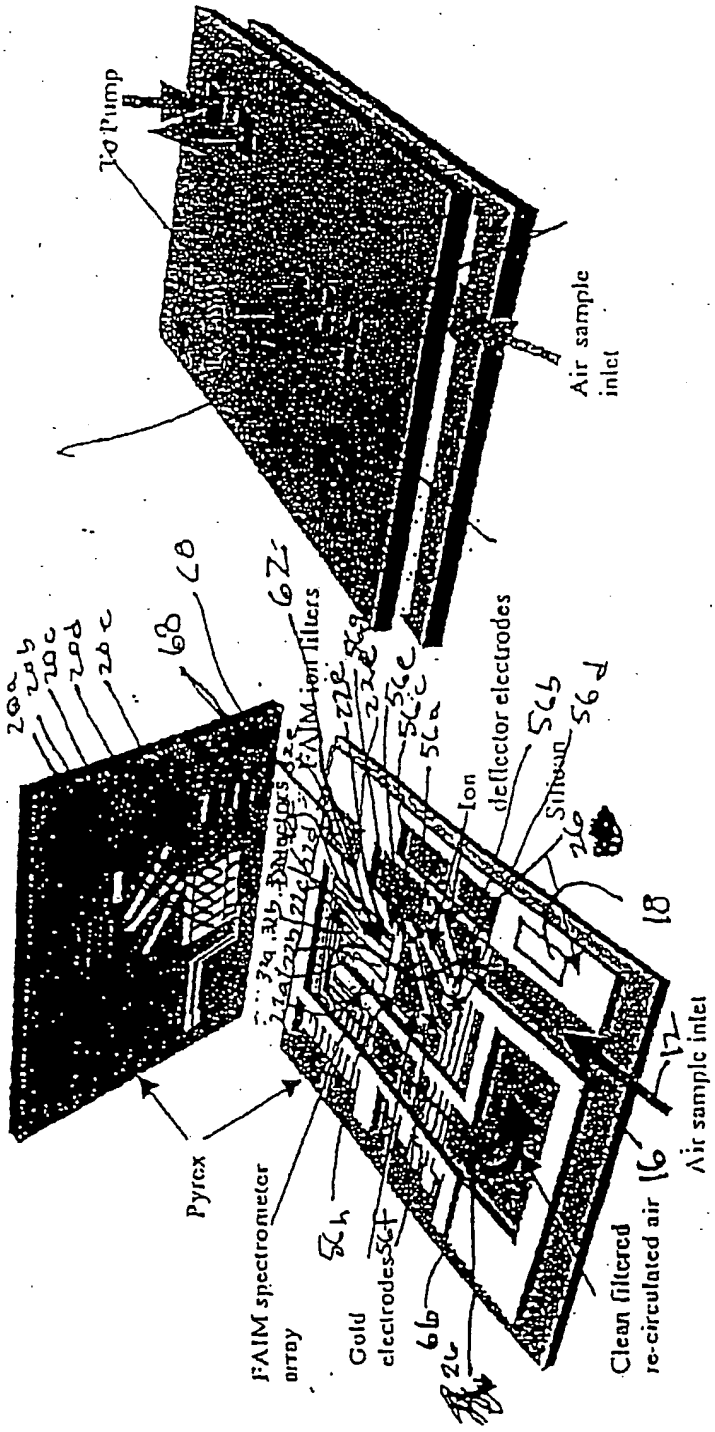
To Pump
Air sample inlet
Ion deflector electrodes
Silicon
FAIM ion filters
Pyrex
FAIM spectrometer array
Gold electrodes
Clean filtered re-circulated air
Air sample inlet
(a)
(b)

FIG. 4

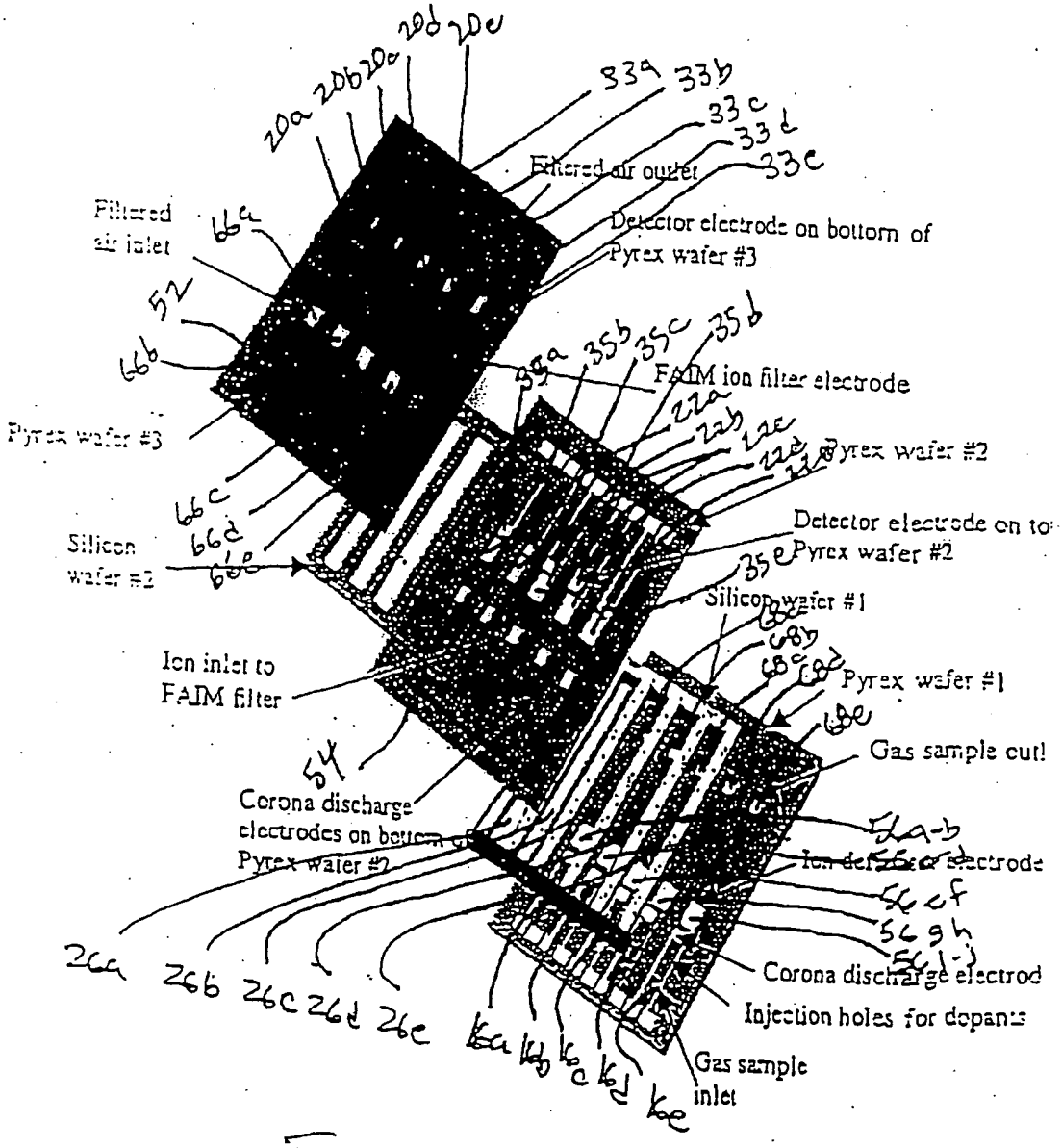
Filtered air inlet
Pyrex wafer #3
Silicon wafer #2
Ion inlet to FAIM filter
Corona discharge electrodes on bottom of Pyrex wafer #2
Filtered air outlet
Detector electrode on bottom of Pyrex wafer #3
FAIM ion filter electrode
Pyrex wafer #2
Detector electrode on to
Pyrex wafer #2
Silicon wafer #1
Pyrex wafer #1
Gas sample out
Corona discharge electrod
Injection holes for dopants
Gas sample inlet

Fig. 7

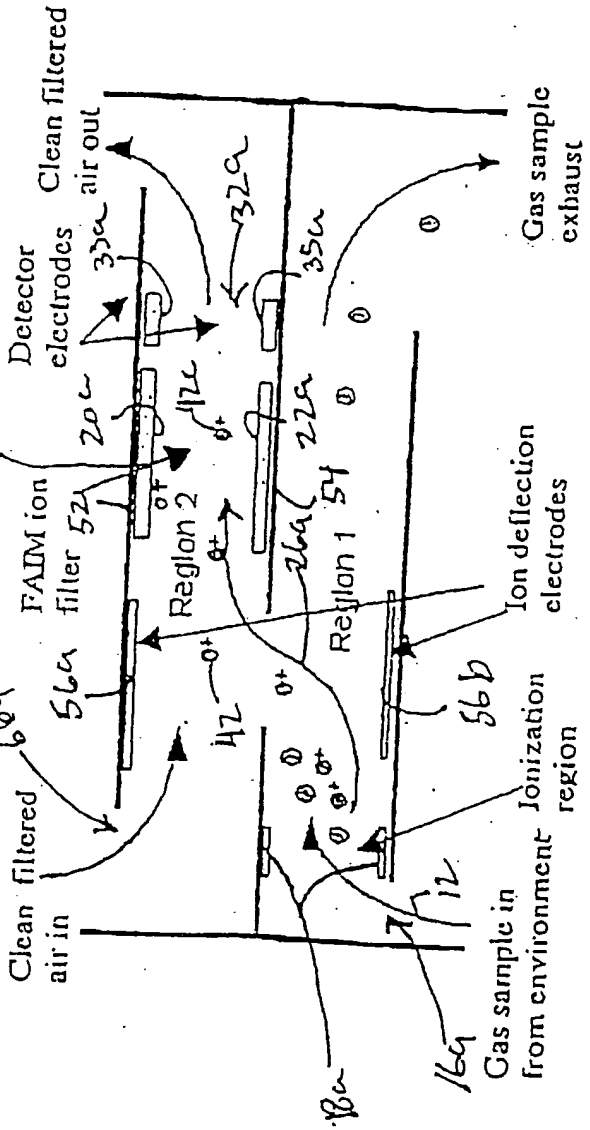
Clean filtered air out
Detector electrodes
Gas sample exhaust
FAIMS ion filter
Region 2
Region 1
Ion deflection electrodes
Clean filtered air in
Ionization region
Gas sample in from environment

FIG. 8

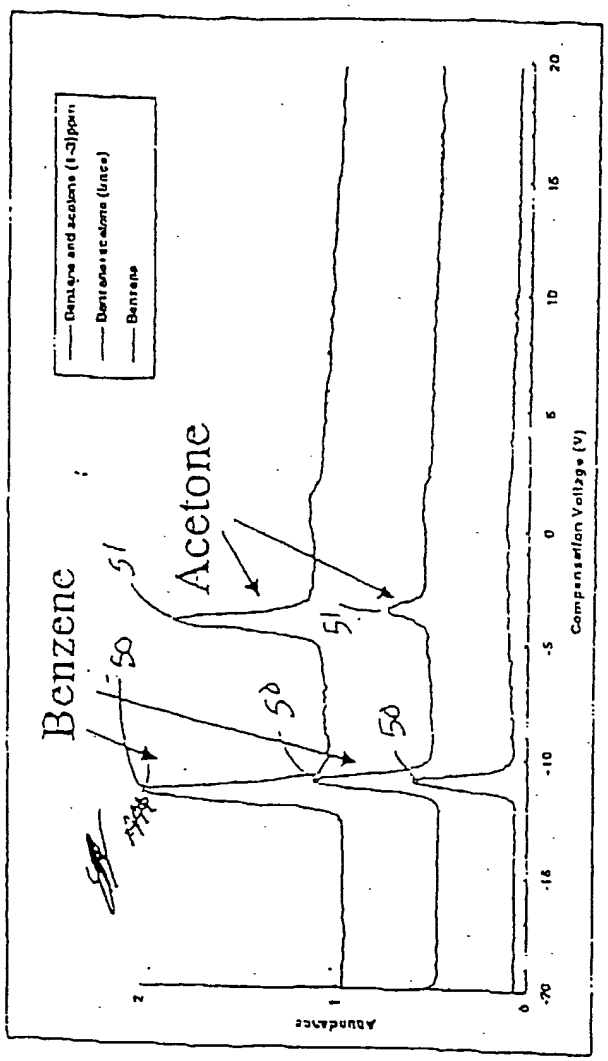

Fig. 3b shows three graphs the top two are for a mixture of acetone and benzene, the bottom is for benzene alone. The graph shows that the acetone peak can be easily distinguished from the benzene peak.

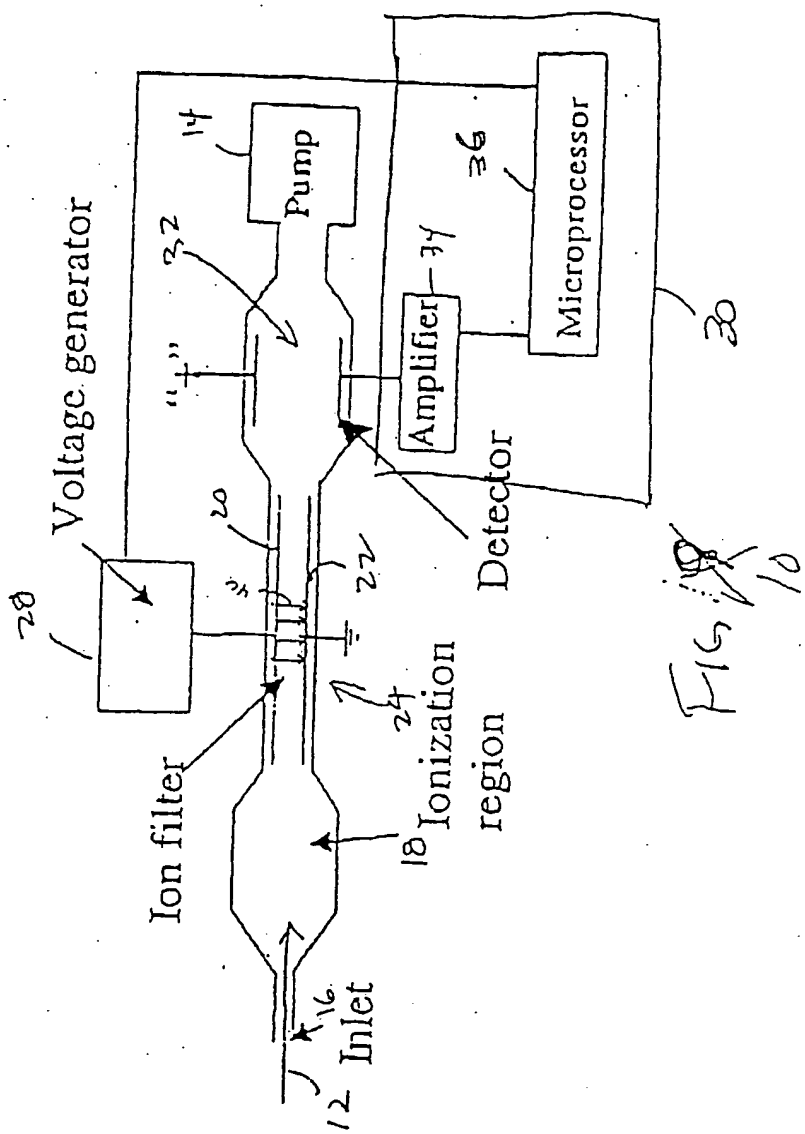
Voltage generator
28
Ion filter
Inlet
12
16
18
Ionization region
24
20
22
"+"
32
Pump
14
Amplifier
34
Detector
Microprocessor
36
30
10

FIG. 1

The figure below shows how the ion trajectory can be altered by changing the excitation voltage duty cycle:

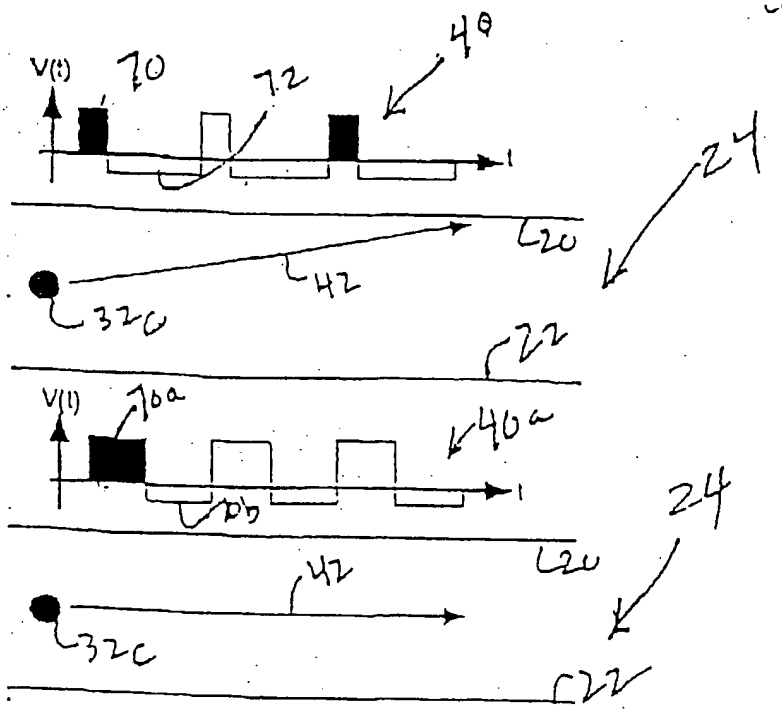

Fig. 11a

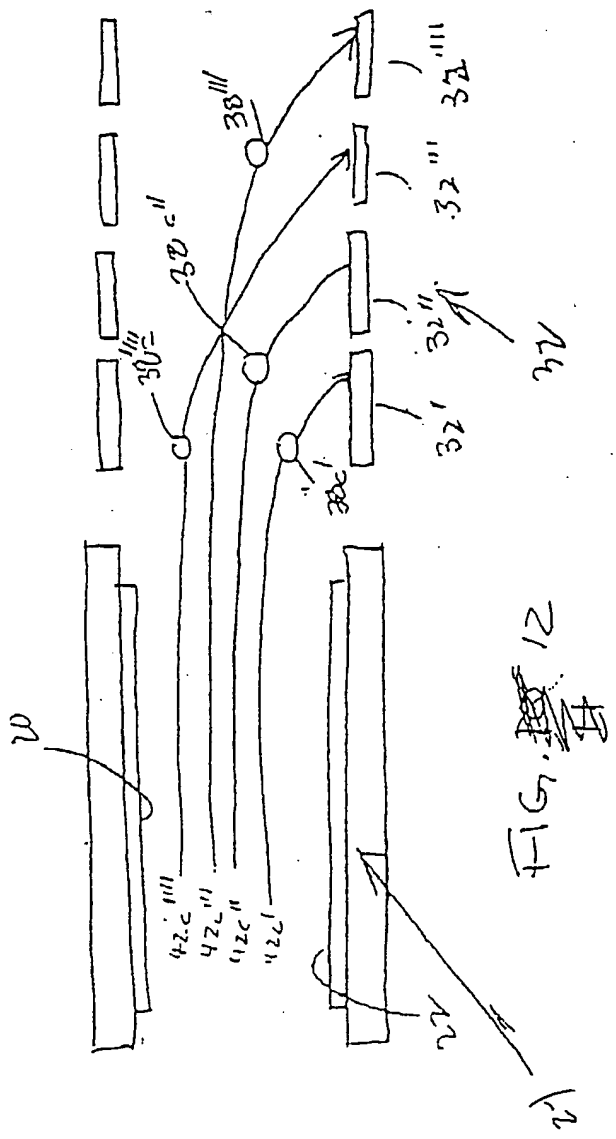

FIG. 12

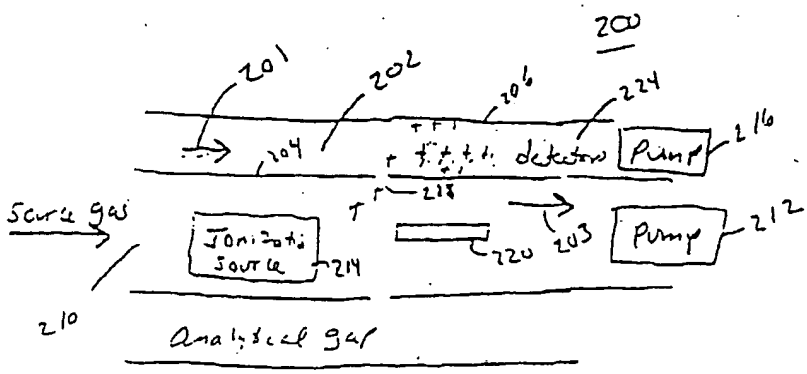

Fig 13 (Prior art)

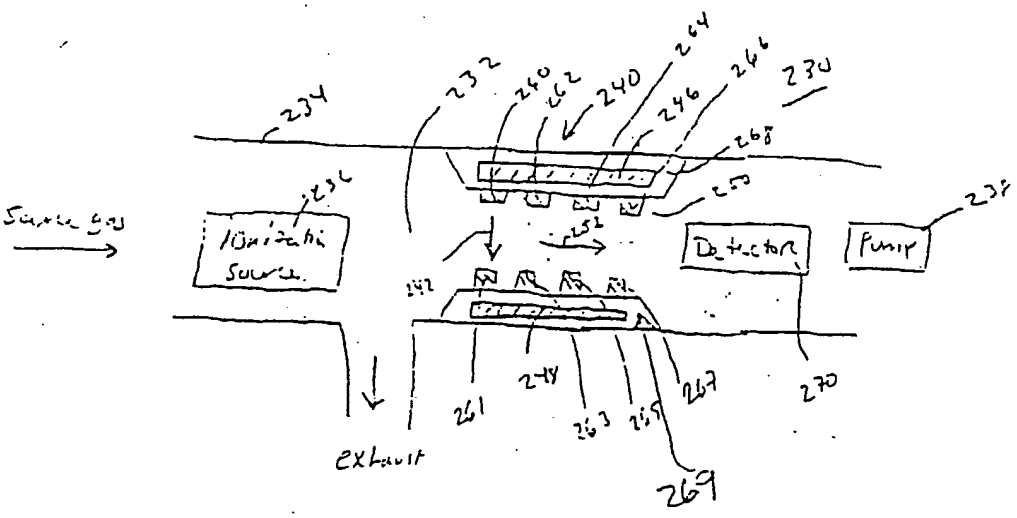

Fig 14.

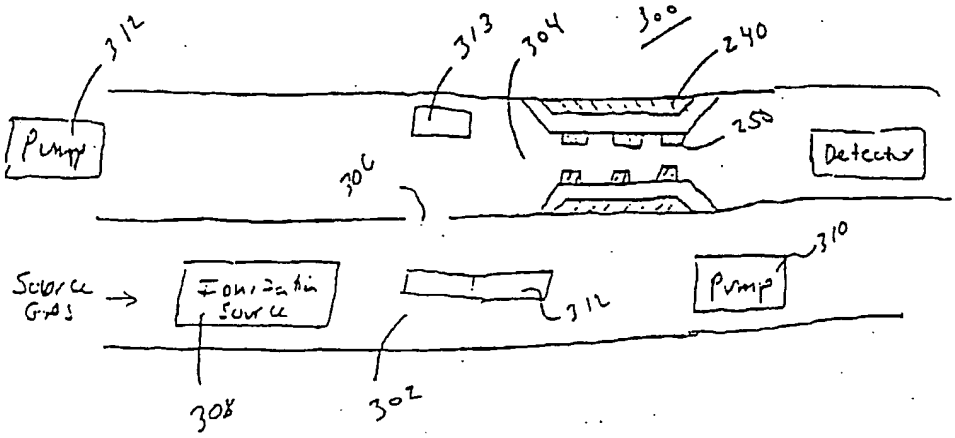
312
313
304
300
240
250
Pump
Detector
306
310
Source Gas
Ionization Source
312
Pump
308
302

Fig 15

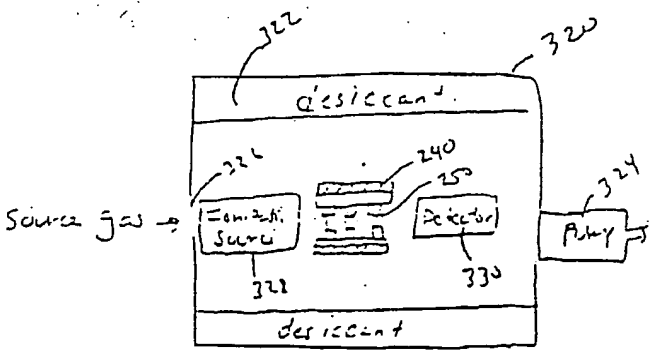
322
320
desiccant
326
240
250
Source gas
Ionizati. Source
Detector
324
Pump
328
330
desiccant

Fig 16

Three options exist for the gas flow in the system: First a low volume flow in the z-direction can be provided. Second no gas flow is present in the ion filter and detector region. Third, a low flow volume of clean filtered air can be provided in the negative z direction to keep the ion filter and detector region free of neutrals.

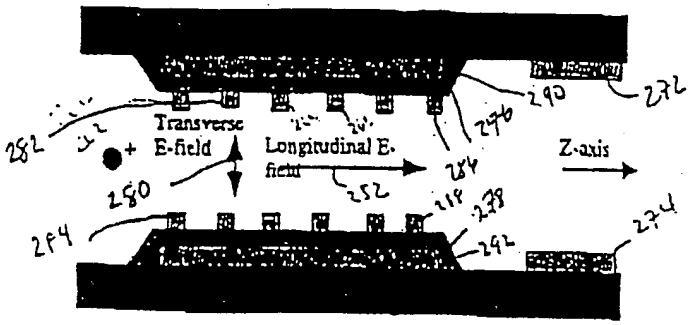

Fig 17

Figure 3.0: Cross-sectional view of FAIM spectrometer with Electric fields in both the transverse and longitudinal directions.

Several designs for the drift tube (ion filter region + detector region) are proposed:

Design #1:
To form this device a metal electrode is deposited on the substrate (possibly pyrex). The electrode is coated with a thin film of insulator (possibly Low Temperature Oxide). The insulator allows a second highly resistive (possibly a resistive ceramic) material to be deposited on top of the insulating layer. Two metal electrodes make contact to this resistive layer and a voltage is dropped across this layer. This voltage produces the longitudinal electric field.

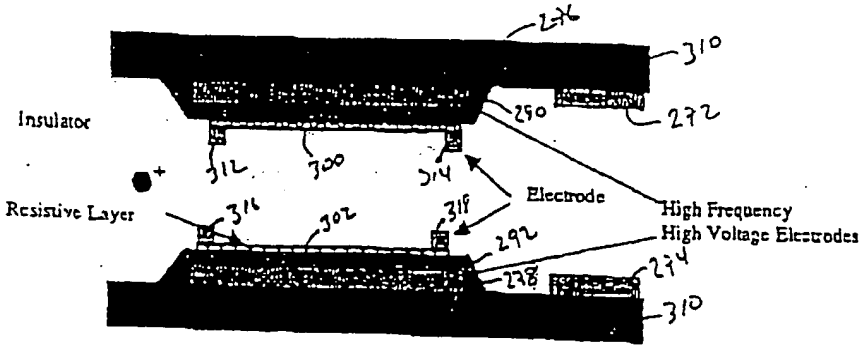

Fig 18

Figure 4.0: Design #1 a resistive layer is used across which a potential is applied Is used to generate the longitudinal (Z-direction) electric field.

Design #2:
In this design instead of a continuous resistive coating a series of metal electrodes are located above the insulator. A resistive divider circuit is built outside of the device to provide a potential gradient across the different electrodes, so that for example, one side of the resistor divider circuit can be at -1000V while the other end at 0 V.

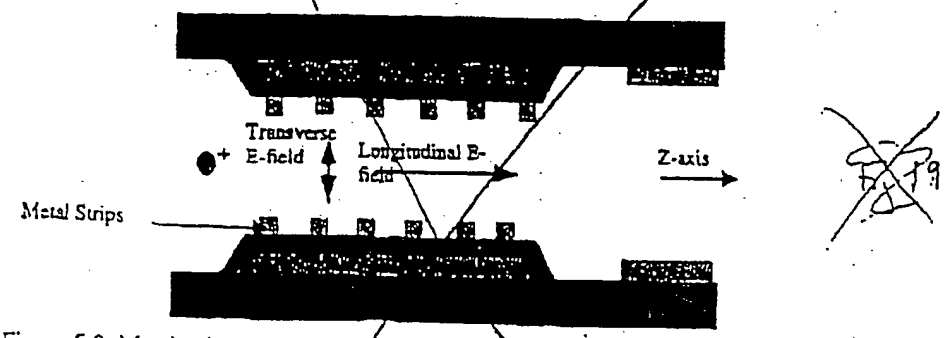

Figure 5.0: Metal strips each at a different potential arranged so that they generate a potential gradient pulling the ions in the z-direction.

Design #3:
Instead of a continuous electrodes and insulators the electrodes are broken up as shown in Figure 6.0. All the high-frequency electrodes are electrically tied together while the longitudinal electrodes have a potential gradient dropped across them. In another scenario the applied voltages to the electrodes can be alternated so that first a voltage is applied to generate a transverse electric field and then the voltage is applied to the other electrodes to generate the longitudinal electric field.

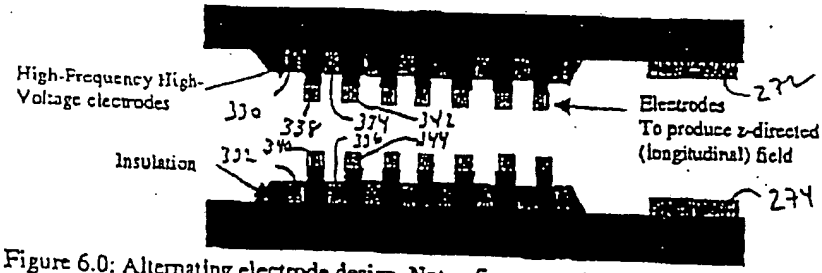

Figure 6.0: Alternating electrode design. Note, figure not drawn to scale. Metal electrodes are much smaller than flow channel gap.

Design #4
In this design only 4 electrodes are used to generate the longitudinal electric field and they are positioned as described in Figure 7.0. The bias on the electrodes is as follows: Electrode 1 and electrode 3 are at the same potential, electrode 2 and electrode 4 are at the same potential. To attract positive ions through the ion filter the voltage on electrodes 2 and 4 is lower than the voltage on electrodes 1 and 3. To move negative ions through

To form this device a metal electrode is deposited on the substrate (possibly Pyrex). The electrode is coated with an insulating film (possibly low temperature oxide or polyimide). The insulator allows a highly resistive material such as Indium Tin Oxide (ITO) to be deposited on top of the insulating layer. Two metal electrodes (#1) make contact to this resistive layer and a voltage is dropped across the layer. This voltage produces the longitudinal electric field. The bottom electrode (#2) provides the asymmetric high frequency, high voltage, electric field. The compensation voltage is superimposed on one of the #1 electrodes.

In another implementation the insulating layer can be replaced with a resistive layer which is more resistive than the ITO film. In yet another implementation the high-frequency high-voltage electrodes can be located exterior to the ion flow channel (on the exterior side of the insulator) while the resistive layer is located on the interior of the ion flow channel. In this configuration the need for a thin insulating layer is eliminated.

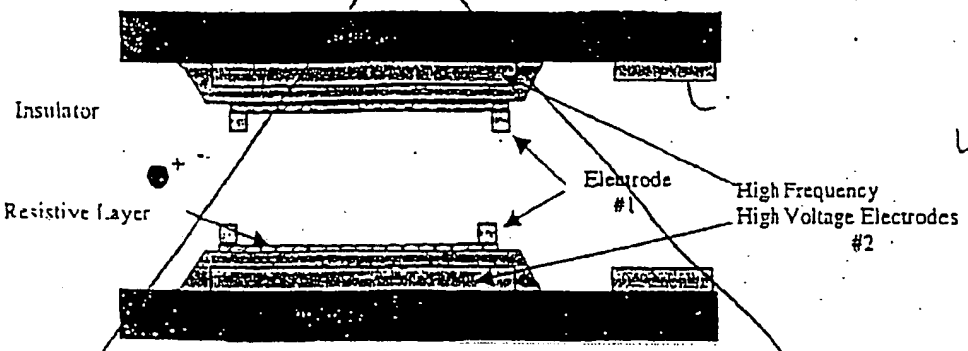

Figure 3.0a: Design #1 a resistive layer across which a potential is applied is used to generate the longitudinal (Z-direction) electric field.

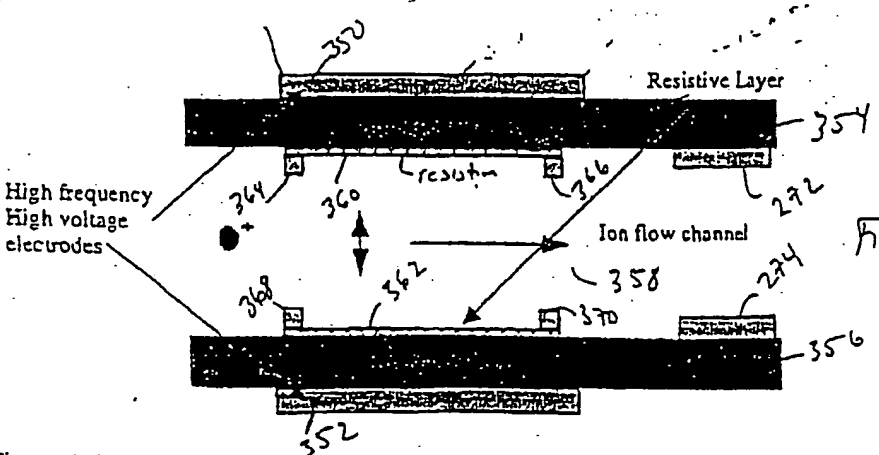

Figure 3.0b: High-frequency high-voltage electrodes located exterior to ion flow channel.

Design #4

A fourth approach is to apply a traveling wave voltage of the form Vcos(omega*t-kz) where k=2*pi/lambda is the wavenumber. Such an imposed traveling wave of voltage has an associated electric field with both transverse and axial components. Traveling wave voltages require polyphase voltage excitations, the simplest being a two phase excitation. A 2 conductor ribbon cable wound around a duct with one conductor excited as Vcos(omega*t) and the other conductor excited as Vsin(omega*t) can produce this traveling wave. Three phase excitations can also be used with a 3 conductor cable. For a planar system, the same effect as a ribbon cable can be achieved using multiply segmented electrodes where each succeeding conductor is excited by a voltage source a fixed phase difference from adjacent electrodes on each side.

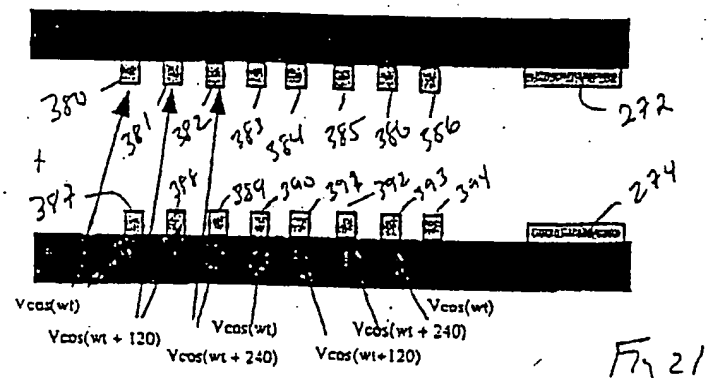

Fig 21

Figure 6.0: Multiply segmented electrodes with a 3 phase excitation.

Note: These drift tube designs can be applied to both the single element FAIM spectrometer and an array of MEMS FAIM spectrometers.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/30921

A. CLASSIFICATION OF SUBJECT MATTER
IPC(7) : H01J 49/00) :
US CL : 250/28, 287
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 250/286, 287

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WEST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,420,424 A (CARNAHAN ET. AL.) 30 MAY 1995 (30.05.95), SEE CLAIMS 1 AND 6.	1-14
A	US 5,455,417 A (SACRISTAN) 03 OCTOBER 1995 (03.10.95), SEE ENTIRE DOCUMENT.	1-14
A	US 5,789,745 A (MARTIN ET. AL.) 04 AUGUST 1998 (04.08.98), SEE ENTIRE DOCUMENT.	1-14
A	US 5,834,771 A (YOON ET. AL.) 10 NOVEMBER 1998 (10.11.98), SEE ENTIRE DOCUMENT.	1-14

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search
28 FEBRUARY 2001

Date of mailing of the international search report
12 MAR 2001

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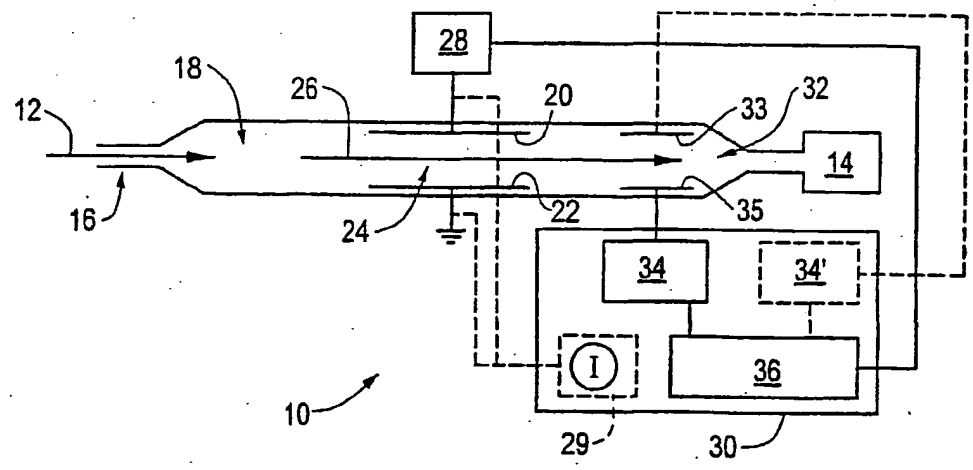
[Continued on next page]

(54) Title: LONGITUDINAL FIELD DRIVEN FIELD ASYMMETRIC ION MOBILITY FILTER AND DETECTION SYSTEM



(57) Abstract: An asymmetric field ion mobility spectrometer (10) with ionization source (18) for ionizing a sample media and creating ions. An ion filter (24) is disposed in the analytical gap downstream from the ionization source for creating an asymmetric electric field to filter the ions. An ion flow generator for creating an electric field in a direction (26) transverse to the asymmetric

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LONGITUDINAL FIELD DRIVEN FIELD ASYMMETRIC ION MOBILITY FILTER AND DETECTION SYSTEM

RELATED CASES

This application is a Continuation-In-Part Application of Application Serial No. 09/358,132 filed July 21, 1999.

FIELD OF INVENTION

This invention relates to a Longitudinal Field Driven Field Asymmetric Ion Mobility (FAIM) filter, and more particularly to a micromachined spectrometer.

BACKGROUND OF INVENTION

The ability to detect and identify explosives, drugs, chemical and biological agents as well as air quality has become increasingly more critical given increasing terrorist and military activities and environmental concerns. Previous detection of such agents was accomplished with conventional mass spectrometers, time of flight ion mobility spectrometers and conventionally machined FAIM spectrometers.

Mass spectrometers are very sensitive, highly selective and provide a fast response time. Mass spectrometers, however, are large and require significant amounts of power to operate. They also require a powerful vacuum pump to maintain a high vacuum in order to isolate the ions from neutral molecules and permit detection of the selected ions, and are also very expensive.

Another spectrometric technique which is less complex is time of flight

ion mobility spectrometry which is the method currently implemented in most portable chemical weapons and explosives detectors. The detection is based not solely on mass, but on charge and cross-section of the molecule as well. However, because of these different characteristics, molecular species identification is not as conclusive and accurate as the mass spectrometer. Time of flight ion mobility spectrometers typically have unacceptable resolution and sensitivity limitations when attempting to reduce their size, that is a drift tube length less than 2 inches. In time of flight ion mobility, the resolution is proportional to the length of the drift tube. The longer the tube the better the resolution, provided the drift tube is also wide enough to prevent all ions from being lost to the side walls due to diffusion. Thus, fundamentally, miniaturization of time of flight ion mobility systems leads to a degradation in system performance. While conventional time of flight devices are relatively inexpensive and reliable, they suffer from several limitations. First, the sample volume through the detector is small, so to increase spectrometer sensitivity either the detector electronics must have extremely high sensitivity, requiring expensive electronics, or a concentrator is required, adding to system complexity. In addition, a gate and gating electronics are usually needed to control the injection of ions into the drift tube.

FAIM spectrometry was developed in the former Soviet Union in the 1980's. FAIM spectrometry allows a selected ion to pass through a filter while blocking the passage of undesirable ions. One prior FAIM spectrometer was large and expensive, e.g., the entire device was nearly a cubic foot in size and cost over $25,000. These systems are not suitable for use in applications

requiring small detectors. They are also relatively slow, taking as much as one minute to produce a complete spectrum of the sample gas, are difficult to manufacture and are not mass producible.

Moreover, the pumps required to draw a sample medium into the spectrometer and to provide a carrier gas can be rather large and consume large amounts of power. And, the carrier gas necessarily must flow in the same direction as the ions which requires a structure which separates the analytical gap from the ionization source.

BRIEF SUMMARY OF THE INVENTION

It is therefore an object of this invention to provide a FAIM filter and detection system which can more quickly and accurately control the flow of selected ions to produce a sample spectrum than conventional FAIM devices.

It is a further object of this invention to provide such a filter and detection system which can detect multiple pre-selected ions without having to sweep the bias voltage.

It is a further object of this invention to provide such a filter and detection system which can even detect selected ions without a bias voltage.

It is a further object of this invention to provide such a filter and detection system which can detect ions spatially based on the ions' trajectories.

It is a further object of this invention to provide such a filter and detection system which has a very high resolution.

It is a further object of this invention to provide such a filter and detection system which can detect selected ions faster than conventional detection devices.

It is a further object of this invention to provide such a filter and detection system which has a sensitivity of parts per billion to parts per trillion.

It is a further object of this invention to provide such a filter and detection system which may be packaged in a single chip.

It is a further object of this invention to provide such a filter and detection system which is cost effective to implement and produce.

It is a further object of this invention to provide such a filter and detection system which does not require the high flow rate, high power consumption pumps normally associated with spectrometers.

This invention results from the realization that the pumps used to draw a sample media such as a gas into a FAIM spectrometer and to provide a flow of carrier gas can be made smaller or even eliminated in part by the incorporation of an ion flow generator which creates a longitudinal electric field in the direction of the intended ion travel path to propel the ions to the detector and through the transversely directed asymmetric electric field which acts as an ion filter.

The result is the ability to incorporate lower cost, lower flow rate, and smaller, even micromachined pumps; a decrease in power usage; the ability to now apply clean filtered gas (e.g., dehumidified air) in a direction opposite the direction of ion travel to eliminate ion clustering and the sensitivity of the spectrometer to humidity. Separate flow paths for the source gas and the clean filtered gas are no longer required thus reducing the structure required to maintain separate flow paths taught by the prior art. Moreover, if an electrospray nozzle is used as the ionization source, the electrodes used to create the fine droplets of solvent can be eliminated because the electrodes which create the longitudinal and transverse electric fields

function to both transport the ions and to create the fine spray of solvent droplets.

The spectrometer can be made extremely small, if required, and used in chemical and military applications, as a filter for a mass spectrometer, as a detector for a gas chromatograph, as a front end to a time of flight ion mobility spectrometer for increased resolution or as a filter for a flexural plate wave device.

The invention results from the further realization that an extremely small, accurate and fast FAIM filter and detection system can be achieved by defining a flow path between a sample inlet and an outlet using a pair of spaced substrates and disposing an ion filter within the flow path, the filter including a pair of spaced electrodes, one electrode associated with each substrate and a controller for selectively applying a bias voltage and an asymmetric periodic voltage across the electrodes to control the path of ions through the filter.

The invention results from the further realization that by providing an array of filters, each filter associated with a different bias voltage, the filter may be used to detect multiple selected ions without sweeping the bias voltage.

The invention results from the further realization that by varying the duty cycle of the periodic voltage, no bias voltage is required.

The invention results from the further realization that by segmenting the detector, ion detection may be achieved with greater accuracy and resolution by detecting ions spatially according to the ions' trajectories as the ions exit the filter.

This invention features an ion mobility spectrometer comprising an ionization source for ionizing a sample media and creating ions; an analytical gap; an ion filter disposed in the analytical gap downstream from the ionization source for creating an asymmetric electric field to filter the ions; an ion flow generator for

creating an electric field in a direction transverse to the asymmetric electric field which is in the longitudinal direction for propelling ions through the asymmetric electric field; and an ion detector for sensing ions not filtered by the ion filter.

The ion detector is typically located proximate to the ion flow generator. The spectrometer may be a radiation source, an ultraviolet lamp, a corona discharge device, or an electrospray nozzle.

The ion filter is preferably connected to an electric controller for applying a bias voltage and an asymmetric periodic voltage to the ion filter. The ion filter typically includes a pair of spaced electrodes for creating an asymmetric electric field between them. The ion flow generator typically includes a plurality of spaced discrete electrodes insulated from these electrodes for creating the transverse direction electric field which propels the ions through the asymmetric electric field and to the detector.

Alternatively, the ion flow generator includes spaced resistive layers and a voltage is applied along each layer to create the longitudinally directed electric field which propels the ions through the asymmetric electric field and to the detector.

In another embodiment, the ion filter includes a first plurality of discrete electrodes electrically connected to an electric controller which applies an asymmetric periodic voltage to them. The ion flow generator includes a second plurality of discrete electrodes dispersed among the electrodes of the ion filter and connected to a voltage source which applies a potential gradient along the second plurality of discrete electrodes.

The analytical gap typically is enclosed by a housing. The ion filter

includes electrodes on an inside surface of the housing and the ion flow generator includes electrodes proximate but insulated with respect to the ion filter electrodes. The ion detector also includes electrodes on an inside surface of the housing proximate to the ion filter and the ion flow generator.

The analytical gap is typically enclosed by a housing, the ion filter may include electrodes on an outside surface of the housing and the ion flow generator then includes resistive layers on an inside surface of the housing. A voltage is applied along each resistive layer to create a longitudinal electric field. Alternatively, the ion filter and the ion flow generator are combined and include a series of discrete conductive elements each excited by a voltage source at a different phase.

BRIEF DESCRIPTION OF THE DRAWINGS

Other objects, features and advantages will occur to those skilled in the art from the following description of a preferred embodiment and the accompanying drawings, in which:

Fig. 1 is a schematic block diagram of the micromachined filter and detection system according to the present invention;

Fig. 2 is a schematic representation of the ions as they pass through the filter electrodes of Fig. 1 toward the detector;

Fig. 3A is a graphical representation of the bias voltage required to detect acetone and the sensitivity obtainable;

Fig. 3B is a representation, similar to Fig. 3A, of the bias voltage required to detect Diethyl methyl amine;

Fig. 4 is a cross sectional view of the spaced, micromachined filter according to the present invention;

Fig. 5 is a three dimensional view of the packaged micromachined filter and detection system, including fluid flow pumps, demonstrating the miniaturized size which may be realized;

Fig. 6 is an exploded view of one embodiment according to the present invention in which an array of filters and detectors are disposed in the same flow path;

Fig. 7 is an exploded view, similar to Fig. 6, in which the array of filters is stacked and one filter and detector is associated with a single flow path.

Fig. 8 is a cross sectional representation of a single flow path of the arrayed filter and detector system of Fig. 7;

Fig. 9 is graphical representation demonstrating identification of individual chemicals from a mixture of benzene and acetone;

Fig. 10 is a schematic block diagram, similar to Fig. 1, in which the filter is not compensated by a bias voltage and the duty cycle of the periodic voltage is instead varied to control the flow of ions through the filter;

Fig. 11 is a graphical representation of an asymmetric periodic voltage having a varying duty cycle which is applied to the filter of Fig. 9 to filter selected ions without a bias voltage;

Fig. 12 is a schematic diagram of a filter and detector system in which the detector is segmented to spatially detect ions as they exit the filter;

Fig. 13 is a schematic view of a typical prior art spectrometer;

Fig. 14 is a schematic view of one embodiment of the longitudinal field

driven ion mobility spectrometer of the subject invention;

Fig. 15 is a schematic view of another embodiment of the longitudinal field driven ion mobility spectrometer of this invention;

Fig. 16 is a schematic view of another embodiment of the longitudinal field driven ion mobility spectrometer of this invention;

Fig. 17 is a schematic view of the ion filter, detector, and ion flow generator portion of the spectrometer of this invention;

Fig. 18 is a schematic view of another embodiment of the ion filter, detector, and ion flow generator portion of a spectrometer according to this invention;

Fig. 19 is a schematic view of another embodiment of the ion filter, detector, and ion flow generator portion of a spectrometer according to this invention;

Figs. 20 is a schematic view of another embodiment of the ion filter, detector, and ion flow generator portion of a spectrometer according to this invention; and

Fig. 21 is a schematic view of another embodiment of the ion filter, detector, and ion flow generator portion of a spectrometer according to this invention.

PREFERRED EMBODIMENT

FAIM spectrometer 10, Fig. 1, operates by drawing a gas, indicated by arrow 12, via pump 14, through inlet 16 into ionization region 18. The ionized

gas is passed between parallel electrode plates 20 and 22, which comprise ion filter 24, following flow path 26. As the gas ions pass between plates 20 and 22, they are exposed to an electric field between electrode plates 20 and 22 induced by a voltage applied to the plates by voltage generator 28 in response to electronic controller 30. The electric field produced preferably is asymmetric and oscillates in time.

As ions pass through filter 24, some are neutralized by plates 20 and 22 while others pass through and are sensed by detector 32. Detector 32 includes a top electrode 33 at a predetermined voltage and a bottom electrode 35, typically at ground. Top electrode 33 deflects ions downward to electrode 35. However, either electrode may detect ions depending on the ion and the voltage applied to the electrodes. Moreover, multiple ions may be detected by using top electrode 33 as one detector and bottom electrode 35 as a second detector. Electronic controller 30 may include, for example, amplifier 34 and microprocessor 36. Amplifier 34 amplifies the output of detector 32, which is a function of the charge collected by electrode 35 and provides the output to microprocessor 36 for analysis. Similarly, amplifier 34', shown in phantom, may be provided where electrode 33 is also utilized as a detector.

As ions 38, Fig. 2, pass through alternating asymmetric electric field 40, which is transverse to gas flow 12, electric field 40 causes the ions to "wiggle" along paths 42a, 42b and 42c. Time varying voltage V is typically in the range of ± (1000-2000) volts and creates electric field 40 with a maximum field strength of 40,000 V/cm. The path taken by a particular ion is a function of its mass, size, cross-section and charge. Once an ion reaches electrode 20 or 22, it is

neutralized. A second, bias or compensation field 44, typically in the range of ± 2000 V/cm due to a ± 100 volt dc voltage, is concurrently induced between electrodes 20 and 22 by a bias voltage applied to plates 20 and 22, also by voltage generator 28, Fig. 1, in response to microprocessor 36 to enable a preselected ion species to pass through filter 24 to detector 32. Compensation field 44 is a constant bias which offsets alternating asymmetric field 40 to allow the preselected ions, such as ion 38c to pass to detector 32. Thus, with the proper bias voltage, a particular species of ion will follow path 42c while undesirable ions will follow paths 42a and 42b to be neutralized as they encounter electrode plates 20 and 22.

The output of FAIM spectrometer 10 is a measure of the amount of charge on detector 32 for a given bias electric field 44. The longer the filter 24 is set at a given compensation bias voltage, the more charge will accumulate on detector 32. However, by sweeping compensation voltage 44 over a predetermined voltage range, a complete spectrum for sample gas 12 can be achieved. The FAIM spectrometer according to the present invention requires typically less than thirty seconds and as little as one second to produce a complete spectrum for a given gas sample.

By varying compensation bias voltage 44 the species to be detected can be varied to provide a complete spectrum of the gas sample. For example, with a bias voltage of

-3.5 volts acetone was detected as demonstrated by concentration peaks 46, Fig. 3A in concentrations as low as 83 parts per billion. In contrast, at a bias voltage of -6.5 volts, diethyl methyl amine, peaks 48, Fig. 3B, was detected in

concentrations as low as 280 parts per billion.

Filter 24, Fig. 4, is on the order of one inch in size. Spectrometer 10 includes spaced substrates 52 and 54, for example glass such as Pyrex® available from Corning Glass, Corning, N.Y., and electrodes 20 and 22, which may be for example gold, titanium, or platinum, mounted or formed on substrates 52 and 54, respectively. Substrates 52 and 54 are separated by spacers 56a and 56b which may be formed by etching or dicing silicon wafer. The thickness of spacers 56a-b defines the distance between electrodes 20 and 22. Moreover, applying the same voltage to silicon spacers 56a-b, typically ± (10-1000 volts dc) transforms spacers 56a and 56b into electrodes which can produce a confining electric field 58, which guides or confines the ions' paths to the center of flow path 26, Fig. 1, in order to obtain a better sample spectrum. To confine the ions, spacer electrodes 56a-b must be set to the appropriate voltages so as to "push" the ions to the center of flow path 26. This increases the sensitivity of the system by preserving more ions so that more ions strike electrodes 33 and 35. However, this is not a necessary limitation of the invention.

To maintain accurate and reliable operation of spectrometer 10, neutralized ions which accumulate on electrode plates 20 and 22 must be purged. This may be accomplished by heating flow path 26. For example, controller 30, Fig. 1, may include current source 29, shown in phantom, which provides, in response to microprocessor 36, a current I to electrode plates 20 and 22 to heat the plates, removing accumulated molecules. Similarly, current I may instead be applied to spacer electrodes 56a and 56 b, Fig. 4, to heat flow path 26 and clean plates 20 and 22.

Packaged FAIM spectrometer 10, Fig. 5, may be reduced in size to one inch by one inch by one inch. Pump 14 is mounted on substrate 52 for drawing a gas sample 12 into inlet 16. Clean dry air may be introduced into flow path 26, Fig. 1, by recirculation pump 14a prior to or after ionization of the gas sample. Electronic controller 30 may be etched into silicon control layer 60 which combines with substrates 52 and 54 to form a housing for spectrometer 10. Substrates 52 and 54 and control layer 60 may be bonded together, for example, using anodic bonding, to provide an extremely small FAIM spectrometer. Micro pumps 14 and 14a provide a high volume throughput which further expedites the analysis of gas sample 12. Pumps 14 and 14a may be, for example, conventional miniature disk drive motors fitted with small centrifugal air compressor rotors or micromachined pumps, which produce flow rates of 1 to 4 liters per minute. One example of pump 14 is available from Sensidyne, Inc., Clearwater, Florida.

While the FAIM spectrometer according to the present invention quickly produces a spectrum for a particular gas sample, the time for doing so may be further reduced with an array of filters 32. FAIM spectrometer 10, Fig. 6, may include filter array 62, a single inlet 16 and single flow path 26. Sample gas 12 is guided by confining electrodes 56a-h to filter array 62 after passing by ionization source 18, which may include an ultraviolet light source, a radioactive device or corona discharge device. Filter array 62 includes, for example, paired filter electrodes 20a-e and 22a-e and may simultaneously detect different ion species by applying a different compensation bias field 44, Fig. 2, to each electrode pair and sweeping each electrode pair over a different voltage range greatly reducing the sweep time. However, array 62 may include any number of filters depending

on the size of the spectrometer. Detector array 64, which includes detectors 32a-e, detects multiple selected ion species simultaneously, thereby reducing the time necessary to obtain a spectrum of the gas sample 12. The electrode pairs share the same asymmetric periodic ac voltage 40.

Clean dry air may be introduced into flow path 26 through clean air inlet 66 via recirculator pump 14a, Fig. 5. Drawing in clean dry air assists in reducing the FAIM spectrometer's sensitivity to humidity. Moreover, if the spectrometer is operated without clean dry air and a known gas sample is introduced into the device, the device can be used as a humidity sensor since the resulting spectrum will change with moisture concentration from the standardized spectrum for the given sample.

However, rather than each filter 32a-e of filter array 62 sharing the same flow path 26, individual flow paths 26a-e, Fig. 7, may be provided so that each flow path has associated with it, for example, inlet 16a , ionization region 18a, confining electrodes 56a', 56b', ion filter electrode pair 20a, 22a, detector electrode pair 33a, 35a and exit port 68a.

In operation, sample gas 12 enters sample inlet 16a, Fig. 8, and is ionized by, for example, a corona discharge device 18a. The ionized sample is guided towards ion filter 24a by confining electrodes 56a and 56b. As ions pass between ion filter electrodes 20a and 22a, undesirable ions will be neutralized while selected ions will pass through filter 24a to be detected by detector 32a.

As shown in Fig. 9, identification of individual constituents of a mixture is demonstrated by the distinct Benzene peaks 50 and the acetone peaks 51 .

It has also been found that a compensation bias voltage is not necessary to

detect a selected specie or species of ion. By varying the duty cycle of the asymmetric periodic voltage applied to electrodes 20 and 22 of filter 24, Fig. 10, there is no need to apply a constant bias voltage to plate electrodes 20 and 22. Voltage generator 28, in response to control electronics 30 varies the duty cycle of asymmetric alternating electric field 40. By varying the duty cycle of periodic electric field 40, Fig. 11, the path of selected ion 32c may be controlled. As an example, rather than a limitation, the duty cycle of field 40 may be one quarter: 25% high, peak 70, and 75% low, valley 72, and ion 38c approaches plate 20 to be neutralized. However, by varying the duty cycle of voltage 40a to 40%, peak 70a, ion 38c passes through plates 20 and 22 without being neutralized. Typically the duty cycle is variable from 10-50% high and 90-50% low. Accordingly, by varying the duty cycle of field 40, an ion's path may be controlled without the need of a bias voltage.

To improve FAIM spectrometry resolution even further, detector 32, Fig. 12, may be segmented. Thus, as ions pass through filter 24 between filter electrodes 20 and 22, the individual ions 38c'-38c'''' may be detected spatially, the ions having their trajectories 42c'-42c'''' determined according to their size, charge and cross section. Thus detector segment 32' will have a concentration of one species of ion while detector segment 32'' will have a different ion species concentration, increasing the spectrum resolution as each segment may detect a particular ion species.

One prior art ion mobility spectrometer 200, Fig. 13, (See U.S. Patent No. 5,420,424) includes analytical gap 202 defined by the space between inner 204 and outer 206 longitudinal electrodes. Sample media, or a source gas is drawn

through inlet 210 via the action of pump 212 and ionized by ionization source 214. A carrier gas is introduced via pump 216 into analytical gap 202. Ions generated by ionization source 214 travel through aperture 218 by the action of electrode 220 and into analytical gap 202 until they reach detector 224.

Such a structure requires two pumps 212 and 216, and separate flow paths 201 and 203 for the source gas and the carrier gas. Thus, prior art mobility spectrometer 200 cannot be made very small, and requires sufficient power to operate pumps 212 and 216.

In the subject invention, the need for pumps 212 and 216 is either eliminated or the pumps are made smaller, even micromachined pumps can be used, for example. Furthermore, separate flow paths for the source gas and the carrier gas are not required and clean filtered gas such as dehumidified air can be introduced to flow in a direction opposite the direction of ion travel to eliminate ion clustering and to improve (lower) the spectrometer's sensitivity to the effects of humidity.

Field asymmetric ion mobility spectrometer 230 according to this invention, Fig. 14, includes analytical gap 232 inside structure 234 which may be a round tube or a small flat housing with walls defining an enclosure. Ionization source 236 ionizes a sample media or gas driven into analytical gap 232 via the action of pump 238 which may be a micromachined pump with a flow rate of much less than the typically required 1-4 liters per minute of the prior art resulting in a power savings of between 1-5 watts over prior art spectrometers.

Ion filter 240 is disposed in analytical gap 232 downstream from ionization source 236 for creating an asymmetric electric field shown by vector

242 to filter ions generated by ionization source 236 as discussed *supra*.

Ion filter 240 typically includes a pair of spaced electrodes 248 and 246 connected to an electric controller which applies a biased voltage and an asymmetric periodic voltage to electrodes 246 and 248, see Figs. 1-2.

Unique to spectrometer 230 is ion flow generator 250 for creating a longitudinal electric field as shown by vector 252. The strength of longitudinal and electric field 252 can be constant in time or space or can vary with time and space and propels ions through asymmetric electric field 242.

In one embodiment, ion flow generator 250 includes discrete electrodes 260, 262, 264, and 266 insulated from electrode 246 and discrete electrodes 248 by insulating mediums 268. In one example, electrode 260 is at 1,000 volts, electrode 266 is at 10 volts and electrodes 262 and 264 are at 500 and 100 volts respectively, although these voltage levels may vary depending on the specific implementation of spectrometer 230. The voltages applied to electrodes 261, 263, 265, and 267 generally match the voltages applied to electrodes 260, 262, 264, and 266, respectively. There may be more or fewer electrodes opposing each other forming ion flow generator 250. Electrode pairs (260, 261), (262, 263), (264, 265), and (266, 267) can also each be a ring electrode as well as discrete planar electrodes.

In any case, the strength of longitudinal electric field 252 propels ions generated by ionization source 236 through asymmetric electric field 242 and towards detector 270 thus eliminating or reducing the flow rate and power requirements of pumps 212 and 216, Fig. 13 of the prior art.

Typically, detector 270 is positioned close to ion flow generator 250 and

electrodes 260, 262, 264, 266, 261, 263, 265, and 267 preferably occupy more or less the same physical space as ion filter 240 electrodes 246 and 248 relative to analytical gap 232.

In another embodiment, spectrometer 300, Fig. 15, includes structure which defines flow path 302 and analytical gap 304 with an opening 306 there between. Source gas is drawn into flow path 302 by pump 310 and ionized by ionization source 308. The ions are deflected through opening 306 and into analytical gap 304 by deflecting electrodes 312 and 313 where the electrodes of ion flow generator 250 and ion filter 240 are disposed. Ion flow generator 250 propels the ions through the asymmetric ion field created by filter 240 as discussed above. In this way, pump 312 need only supply a fairly low flow rate of dehumidified air into analytical gap 304 and no carrier gas flow is required as taught by the prior art.

In another embodiment, a desiccant 322, Fig. 16, is provided in housing 320 and small pump 324 is the only pump required to draw source gas into housing 320 through small orifice 326. Ionization source 328 produces ions which travel through filter 240 aided by the longitudinal electric field created by ion flow generator 250 positioned proximate detector 330.

In one embodiment detector 270, Fig. 14, includes spaced electrodes 272, 274, Fig. 17, similar in construction to electrodes 33 and 35, Fig. 1. The ion filter of Fig. 17 includes spaced electrodes 276 and 278 for creating transverse electric field 280. The ion flow generator includes spaced discrete electrodes as shown for electrodes 282 and 284 and electrodes 286 and 288. Electrodes 282 and 284 may be at 1000 volts and electrodes 286 and 288 may be at 0 volts. Insulating

medium 290 and 292 insulates electrodes 282, 284, 286, and 288 with respect to electrodes 276 and 278. Electrode pairs (282, 284) through (286, 288) or more could also be ring electrodes.

In another embodiment, Fig. 18, the ion filter includes spaced resistive layers 300 and 302 insulated from electrodes 276 and 278 on Pyrex substrate 310 by insulating medium 290 and 292, for example, a low temperature oxide material.

Resistive layers 300 and 302 may be a resistive ceramic material deposited on insulating layers 290 and 292, respectively. Terminal electrodes 312, 314, 316 and 318 make contact with each resistive layer to apply a voltage drop across each resistive layer to generate the longitudinal electric field. Thus, electrodes 312 and 316 may be at 1000 volts while electrodes 314 and 318 may be at 0 volts. This embodiment can be extended to a cylindrical geometry by making electrodes 312 and 316 a ring electrode, electrodes 314 and 318 a ring electrode, and resistive layers 300 and 302 an open cylinder.

In still another embodiment, Fig. 19, the ion filter includes a plurality of high frequency, high voltage electrodes 330, 332, 334 and 336 connected to an electric controller (see Fig. 1) which applies an asymmetric periodic voltage to create an ion filtering electric field and the ion flow generator includes a second plurality of discrete electrodes 338, 340, 342 and 344 dispersed among but insulated from the discrete electrodes of the ion filter as shown and connected to a voltage source which applies a potential gradient across them to generate an ion propelling electric field which is in directed in a direction transverse to the ion filtering electric field.

In still another embodiment, Fig. 20, high frequency electrodes 350, 352 which provide the asymmetric ion filtering electric field are disposed on the outside of walls 354 and 356 made of an insulative material such as PYREX which define analytical gap 358. Resistive layers 360 and 362 may be a resistive ceramic material deposited on the inside of walls insulating walls 354 and 356, respectively. Terminal electrodes 364 and 366, and 368 and 370 make contact with each resistive layer is shown to apply a voltage drop across each resistive layer to generate the ion propelling longitudinal electric field. Thus, electrodes 364 and 368 may each be at 1000 volts while electrodes 366 and 370 are at 0 volts.

In the design shown in Fig. 21, discrete electrodes 380-386 and 387-394 produce an electrical field with both transverse and longitudinal components to both filter and propel the ions. A travelling wave voltage of the form

$$V\cos(wt-kz) \qquad 1$$

where $k = 2\pi/\lambda$ is the wave number has an associated electric field with both transverse and longitudinal components. For a planar system, each succeeding set of opposing electrodes is excited by a voltage source at a fixed phase difference from the voltage source applied to the adjacent set of opposing electrodes.

Thus, electrodes 380 and 387 are excited with a voltage of vcos(wt) while electrodes 381 and 388 are excited with a voltage of vcos (wt + 120) and so on as shown in Fig. 21. Travelling wave voltages require polyphase voltage excitations, the simplest being a two phase excitation. So, a two conductor ribbon could also be wound around a duct defining the analytical gap with one

conductor excited at vcos (wt) and the other conductor excited at vsin (wt). Three phase excitations could be incorporated if the conductor ribbon or tape had three conductors.

The subject designs lend themselves well to the use of an electrospray ionization source nozzle because certain electrodes can function both as the source for the longitudinal electrical field which transports the ions towards the detector electrodes and as the electrodes which create a fine spray of solvent droplets for ionizing the source gas or sample medium.

Thus, in accordance with this invention, pumps 216 and 212, Fig. 13 of the prior art are either eliminated or at least reduced in size and have lower flow rate and power requirements. By the incorporation of an ion flow generator which creates a longitudinal electric field in the direction of the intended ion travel, the ions are propelled to the detector and through the transversely directed asymmetric electric field which acts as an ion filter. In the preferred embodiment, a pump is not required to draw the ionized gas species through the spectrometer drift tube for analysis. Instead, a longitudinal electric field applied along the length of the drift tube can be used to propel the ions down the drift tube through the ion filter to a detector. By eliminating the high flow rate (1-4 liters per minute) pumps used in prior art spectrometers, a significant reduction in power consumption, size, and cost can be realized leading to a truly miniaturized spectrometer on a chip.

A second benefit of this design is that a flow of clean filtered air can be applied in a direction opposite the direction of the motion of the ions. In this way, any neutrals in the sample gas which were not ionized are deflected away

and do not enter the ion analysis region. The result is the elimination of ion clustering problems and the humidity sensitivity of the sensor. Because the flow rates are low, it is possible to incorporate integrated micromachine pumps.

Since only the ions need enter the analysis region, no gas flow is required in the ion filter and detector region. Molecular sieves can be located close to the entrance of this region in order to absorb any neutral molecules in the analysis region and prevent clustering. A separate source of air flow delivered by a pump in the ion filter (analyzer) region is not required in contrast to the prior art which incorporated high flow rate pumps which consumed a relatively large amount of power (1-5 watts) and which added size to the system and/or which could fail. In subject invention, a flow of neutral gas in the same direction as the ion species generated from the sample gas to be analyzed is not required. Instead a flow gas in the opposite direction of the ion flow direction can be applied to keep the ion filter region free of unwanted neutrals and moisture. A higher gas flow rate through the ion filter (drift tube) is not required. Instead, the ions are drawn through the ion filter (drift tube) along the z axis by a longitudinal electric field produced by a small potential gradient in the z direction. In the design shown, Fig. 17, only a low volume flow in the direction of the longitudinal electric field as shown by vector 252 is required to bring the ions proximate to electrodes 282 and 284. No gas flow is required in the ion filter and detector region due to longitudinal electric field 252. Also, if required, a low flow volume of clean filtered air can be provided in a direction opposite the longitudinal electric field to keep the ion filter and detector region free of neutrals. A resistive divider circuit provides a potential gradient across electrodes 282, 284, so that for example,

electrodes 282 and 284 are at 1000 volts while electrodes 286 and 288 are at 0 volts. In the design shown in Fig. 19, all the high frequency electrodes 330, 332, etc. are electrically tied together while the longitudinal field producing electrodes 338, 340 etc. have a potential gradient dropped across them. In one embodiment, the voltages applied to the electrodes can be alternated so that first a voltage is applied to generate the transverse electric field and then a voltage is applied to other electrodes to generate the longitudinal electric field.

Although specific features of the invention are shown in some drawings and not in others, this is for convenience only as each feature may be combined with any or all of the other features in accordance with the invention.

Other embodiments will occur to those skilled in the art and are within the following claims:

What is claimed is:

CLAIMS

1. An asymmetric field ion mobility spectrometer comprising:

an ionization source for ionizing a sample media and creating ions;

an analytical gap;

an ion filter disposed in the analytical gap downstream from the ionization source for creating an asymmetric electric field to filter the ions;

an ion flow generator for creating an electric field transverse to the asymmetric electric field for propelling ions through the asymmetric electric field; and

an ion detector for sensing ions not filtered by the ion filter.

2. The spectrometer of claim 1 in which the ion detector is proximate the ion flow generator.

3. The spectrometer of claim 2 in which the ionization source is a radiation source.

4. The spectrometer of claim 1 in which the ionization source includes an ultraviolet lamp.

5. The spectrometer of claim 1 in which the ionization source includes a corona discharge device.

6. The spectrometer of claim 1 in which the ionization source includes an electrospray nozzle.

7. The spectrometer of claim 1 in which the ion filter is connected to an electric controller for applying a bias voltage and an asymmetric periodic voltage to the ion filter.

8. The spectrometer of claim 1 in which the ion filter includes a pair of spaced electrodes for creating an asymmetric electric field and the ion flow generator includes a plurality of spaced discrete electrodes insulated from the pair of spaced electrodes for creating the transverse direction varying strength electric field.

9. The spectrometer of claim 1 in which the ion flow generator includes spaced resistive layers and a voltage applied along each layer to create a longitudinal electric field.

10. The spectrometer of claim 1 in which the ion filter includes a first plurality of discrete electrodes electrically connected to an electric controller which applies an asymmetric periodic voltage to the first plurality of discrete electrodes and in which the ion flow generator includes a second plurality of discrete electrodes dispersed among the first plurality of discrete electrodes connected to a voltage source which applies a potential gradient along the second plurality of discrete electrodes.

11. The spectrometer of claim 1 in which the analytical gap is enclosed by a housing, the ion filter includes electrodes on an inside surface of the housing and the ion flow generator includes electrodes proximate but insulated with respect to the ion filter electrodes.

12. The spectrometer of claim 11 in which the ion detector includes electrodes on an inside surface of the housing proximate the ion filter and the ion flow generator.

13. The spectrometer of claim 1 in which the analytical gap is enclosed by a housing, the ion filter includes electrodes on an outside surface of the housing and the ion flow generator includes resistive layers on an inside surface of the housing and a voltage is applied along each layer to create a longitudinal electric field.

14. The spectrometric of claim 1 in which the ion filter and the ion flow generator are combined and include a series of discrete conductive elements each excited by a voltage source at a different phase.

AMENDED CLAIMS

[received by the International Bureau on 19 April 2001 (19.04.01);
original claims 8 and 14 amended; new claim 15 added;
remaining claims unchanged (2 pages)]

6. The spectrometer of claim 1 in which the ionization source includes an electrospray nozzle.

7. The spectrometer of claim 1 in which the ion filter is connected to an electric controller for applying a bias voltage and an asymmetric periodic voltage to the ion filter.

8. The spectrometer of claim 1 in which the ion filter includes a pair of spaced electrodes for creating the asymmetric electric field and the ion flow generator includes a plurality of spaced discrete electrodes insulated from the pair of spaced electrodes.

9. The spectrometer of claim 1 in which the ion flow generator includes spaced resistive layers and a voltage applied along each layer to create a longitudinal electric field.

10. The spectrometer of claim 1 in which the ion filter includes a first plurality of discrete electrodes electrically connected to an electric controller which applies an asymmetric periodic voltage to the first plurality of discrete electrodes and in which the ion flow generator includes a second plurality of discrete electrodes dispersed among the first plurality of discrete electrodes connected to a voltage source which applies a potential gradient along the second plurality of discrete electrodes.

11. The spectrometer of claim 1 in which the analytical gap is enclosed by a housing, the ion filter includes electrodes on an inside surface of the housing and the ion flow generator includes electrodes proximate but insulated with respect to the ion filter electrodes.

12. The spectrometer of claim 11 in which the ion detector includes electrodes on an inside surface of the housing proximate the ion filter and the ion flow generator.

13. The spectrometer of claim 1 in which the analytical gap is enclosed by a housing, the ion filter includes electrodes on an outside surface of the housing and the ion flow generator includes resistive layers on an inside surface of the housing and a voltage is applied along each layer to create a longitudinal electric field.

14. The spectrometer of claim 1 in which the ion filter and the ion flow generator are combined and include a series of discrete conductive elements.

15. The spectrometer of claim 1 in which the ion filter is connected to an electric controller for applying a traveling wave voltage.

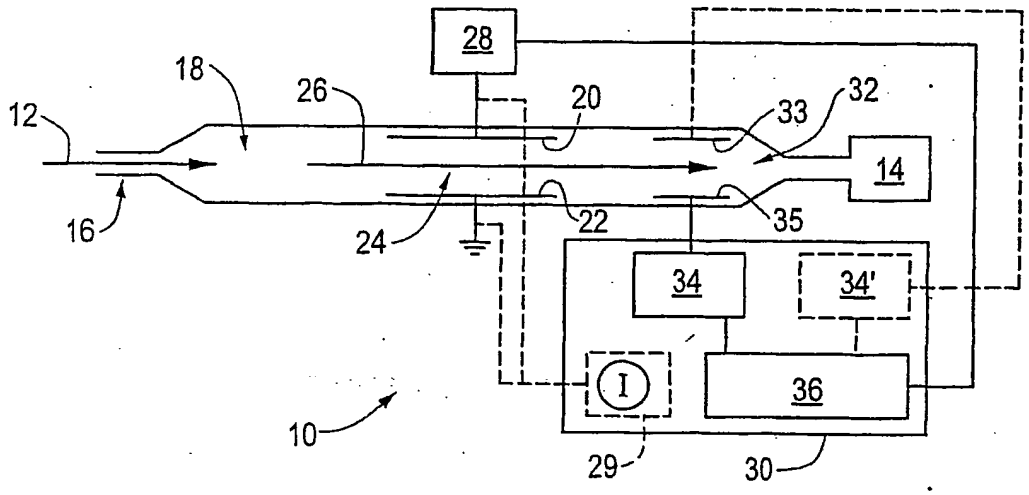

FIG. 1

FIG. 1

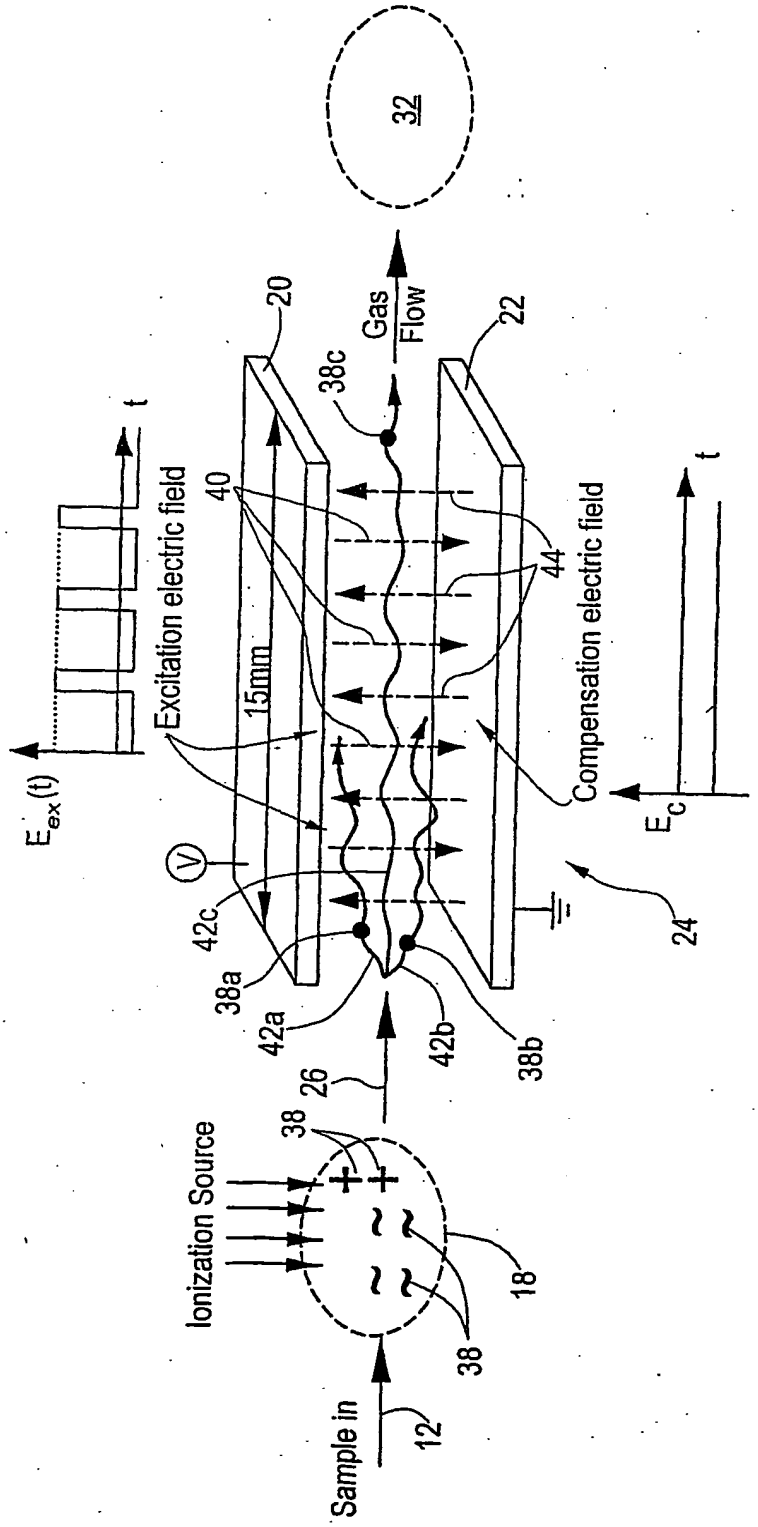
32
Gas Flow
20
22
38c
40
44
15mm
Excitation electric field
Compensation electric field
t
t
$E_{ex}(t)$
E_c
V
42c
38a
42a
42b
38b
26
24
38
Ionization Source
18
38
Sample in
12

FIG.2

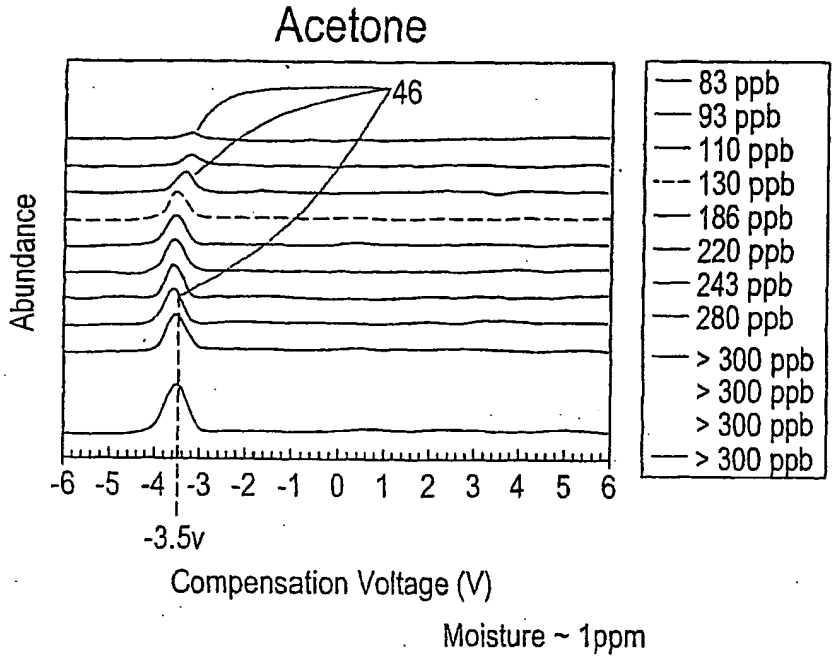
Acetone
46
Abundance
83 ppb
93 ppb
110 ppb
130 ppb
186 ppb
220 ppb
243 ppb
280 ppb
> 300 ppb
> 300 ppb
> 300 ppb
> 300 ppb
-6 -5 -4 -3 -2 -1 0 1 2 3 4 5 6
-3.5v
Compensation Voltage (V)
Moisture ~ 1ppm

FIG. 3A

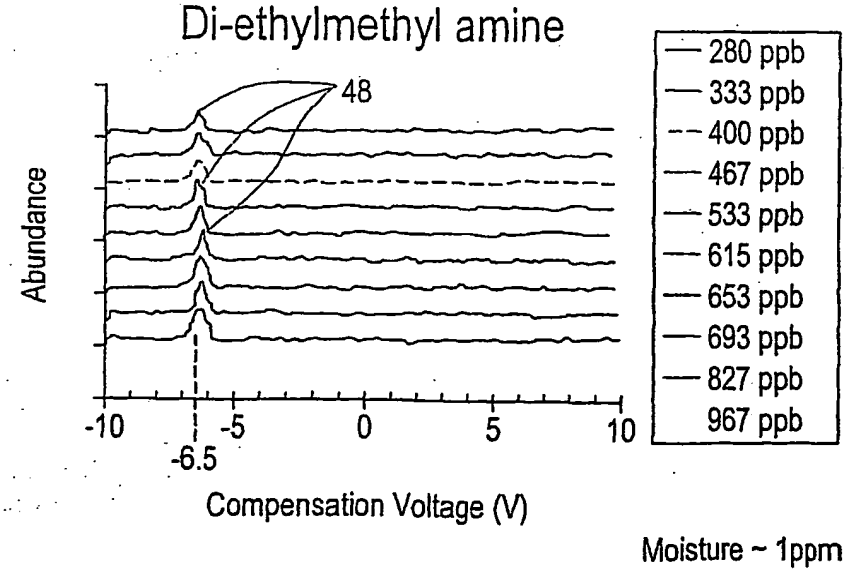
Di-ethylmethyl amine
48
Abundance
280 ppb
333 ppb
400 ppb
467 ppb
533 ppb
615 ppb
653 ppb
693 ppb
827 ppb
967 ppb
-10 -5 0 5 10
-6.5
Compensation Voltage (V)
Moisture ~ 1ppm

FIG. 3B

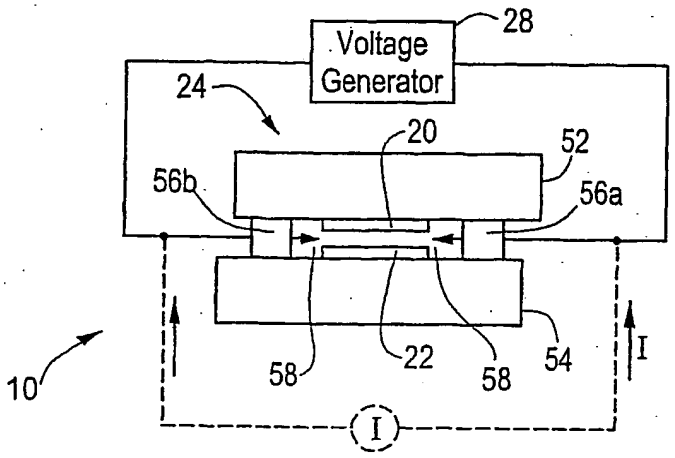
Voltage Generator
28
24
20
52
56b
56a
58
22
58
54
I
10
I

FIG. 4

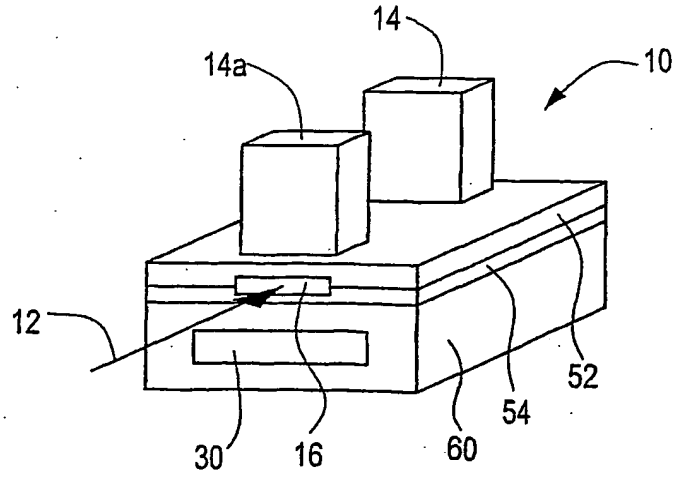
14
14a
10
12
30
16
60
54
52

FIG. 5

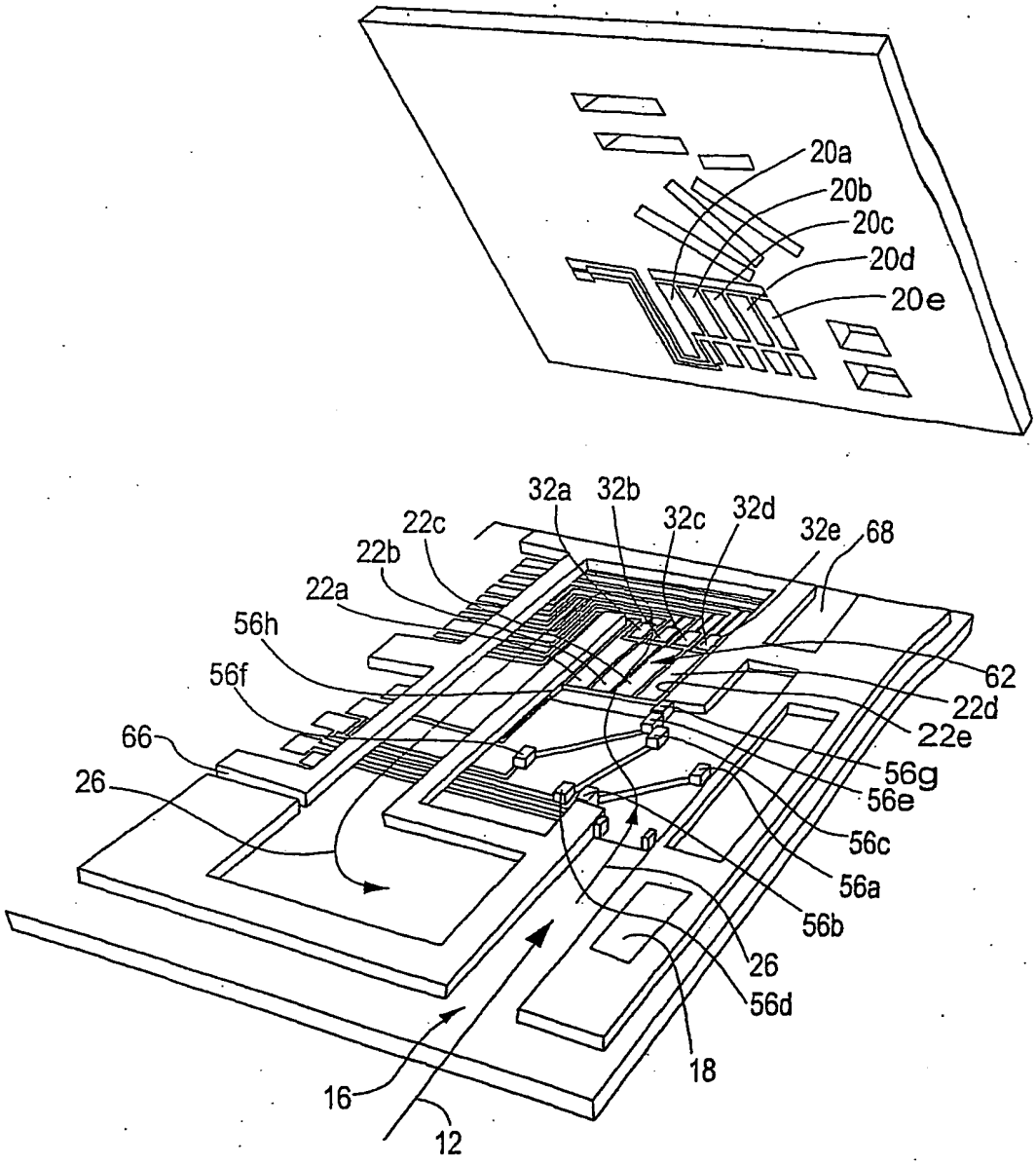
20a
20b
20c
20d
20e
32a
32b
32c
32d
32e
68
22c
22b
22a
56h
56f
66
26
62
22d
22e
56g
56e
56c
56a
56b
26
56d
18
16
12

FIG. 6

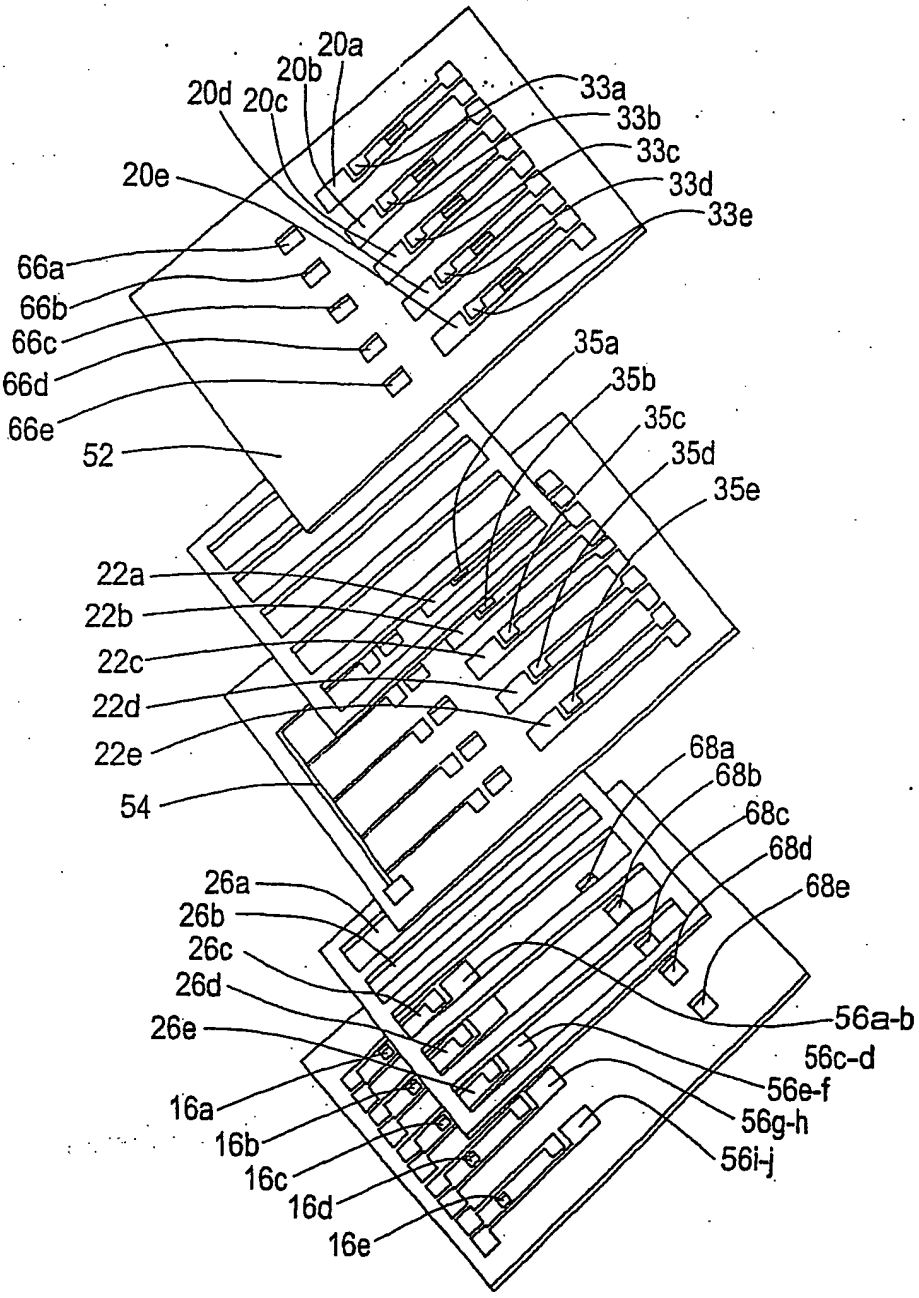
20a
20b
20c
20d
20e
33a
33b
33c
33d
33e
66a
66b
66c
66d
66e
52
35a
35b
35c
35d
35e
22a
22b
22c
22d
22e
54
68a
68b
68c
68d
68e
26a
26b
26c
26d
26e
56a-b
56c-d
56e-f
56g-h
56i-j
16a
16b
16c
16d
16e

FIG. 7

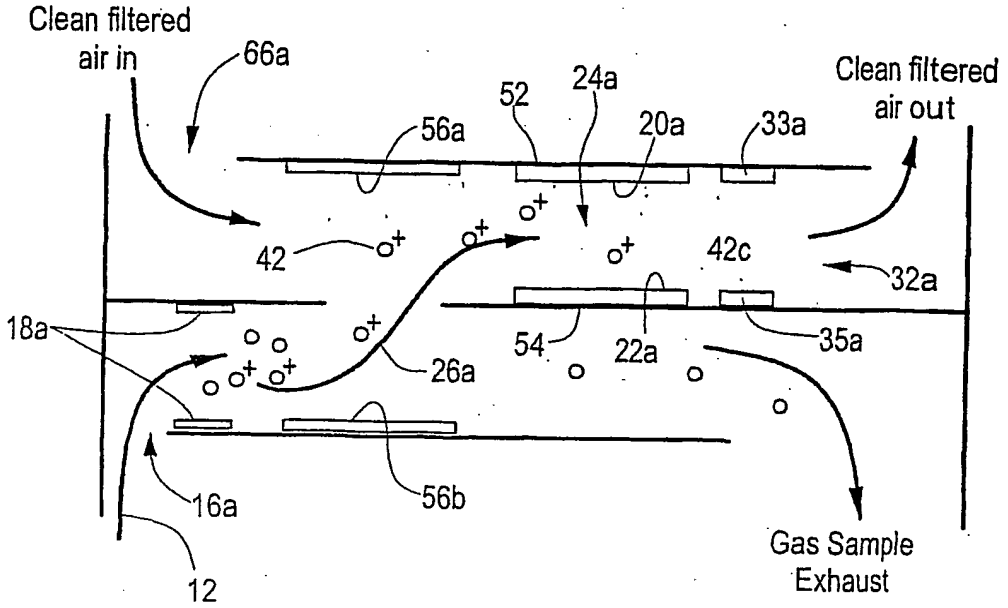
Clean filtered air in
66a
52
24a
Clean filtered air out
56a
20a
33a
42
42c
32a
18a
54
22a
35a
26a
16a
56b
12
Gas Sample Exhaust

FIG. 8

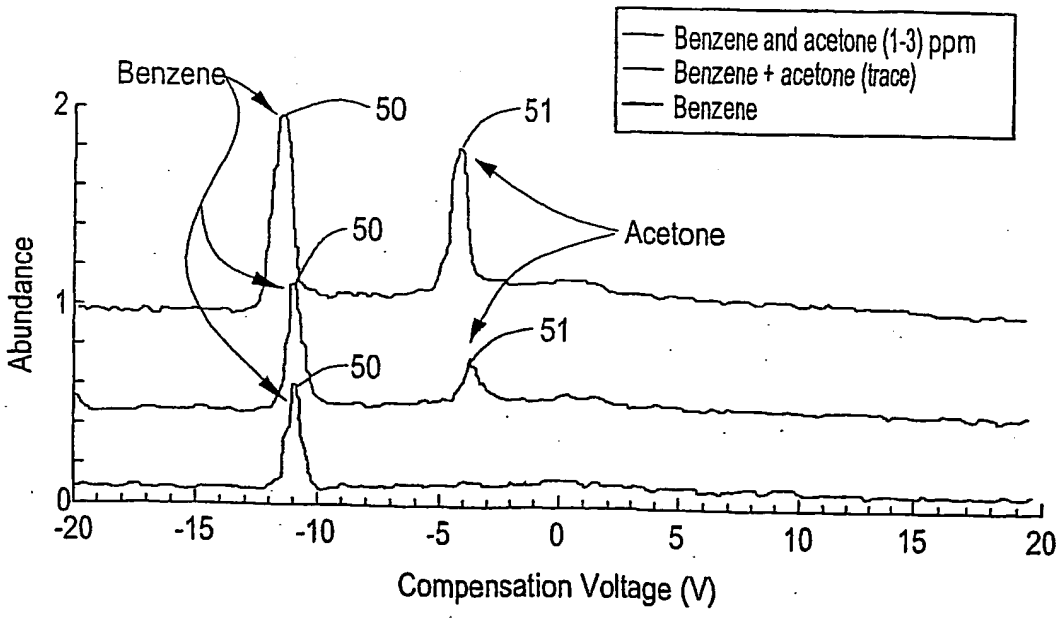
Benzene and acetone (1-3) ppm
Benzene + acetone (trace)
Benzene
Benzene
50
51
Acetone
Abundance
2
1
0
-20
-15
-10
-5
0
5
10
15
20
Compensation Voltage (V)

FIG. 9

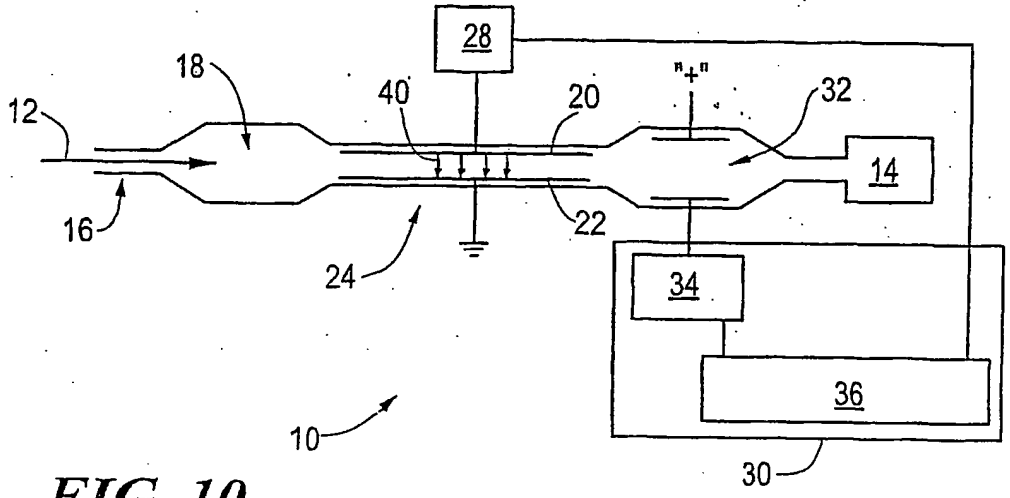
28
18
12
40
20
"+"
32
14
16
22
24
34
36
10
30

FIG. 10

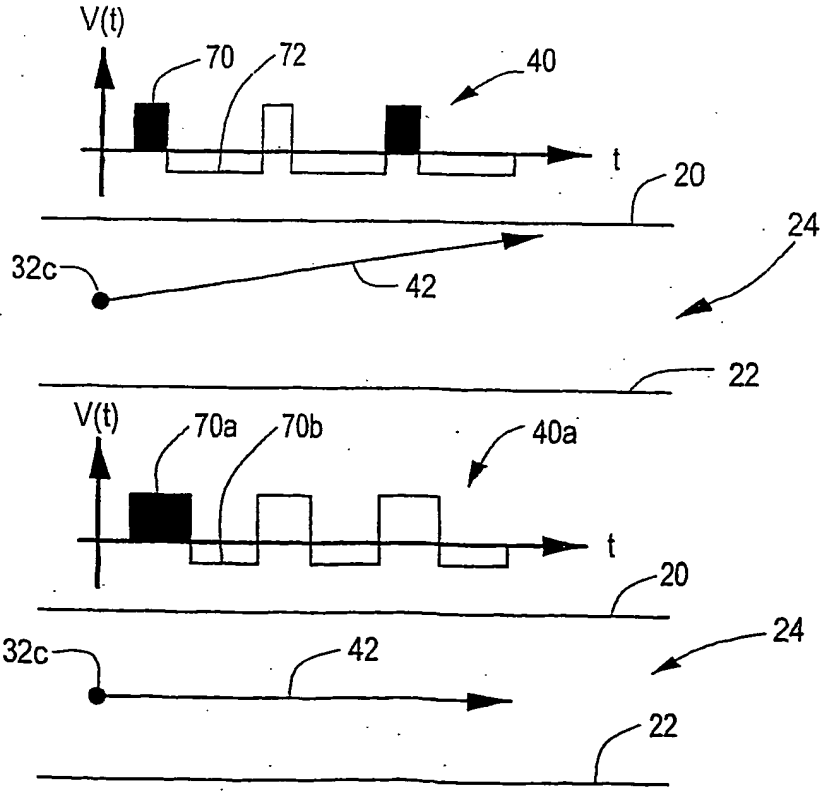
V(t)
70
72
40
t
20
32c
42
24
22
V(t)
70a
70b
40a
t
20
32c
42
24
22

FIG. 11

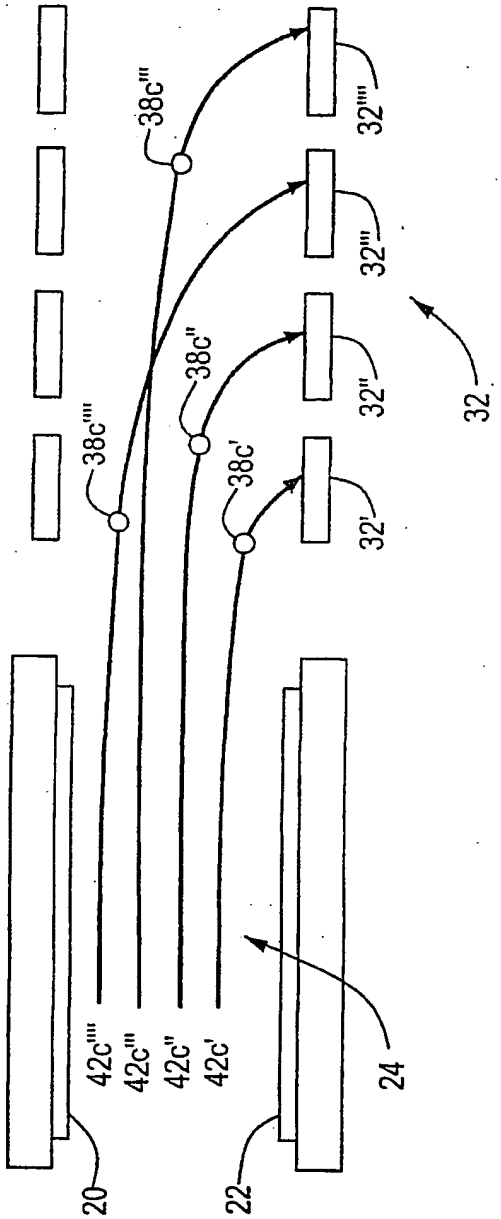

FIG. 12

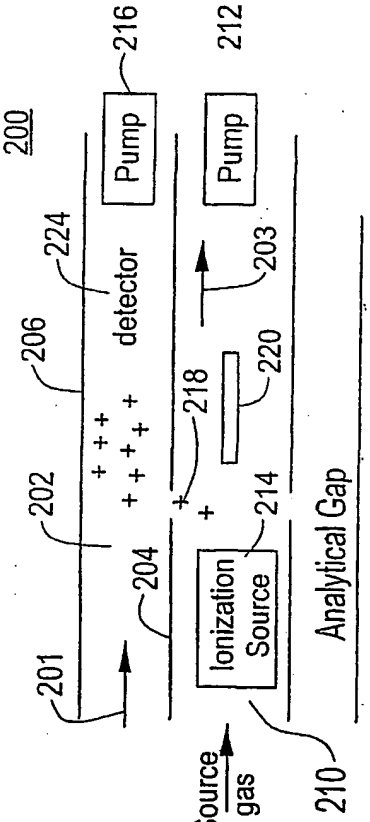

FIG. 13
PRIOR ART

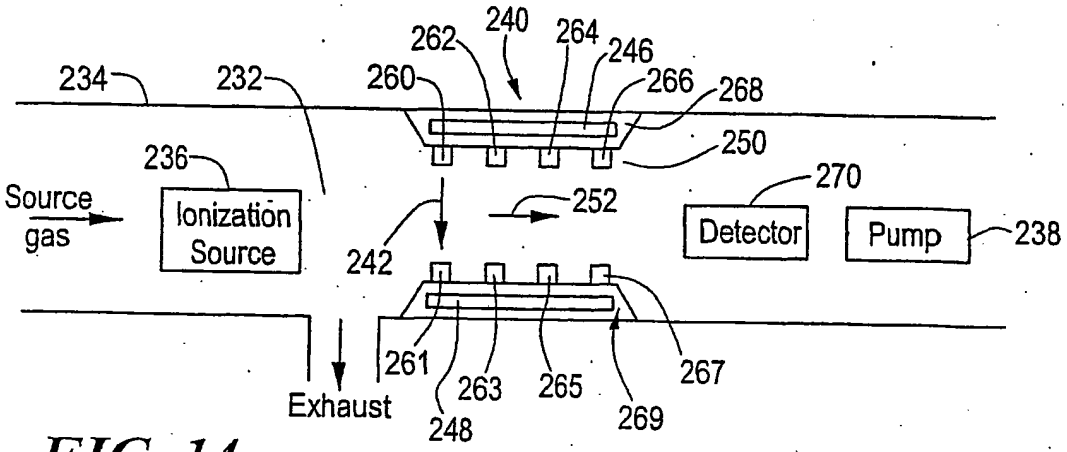

FIG. 14

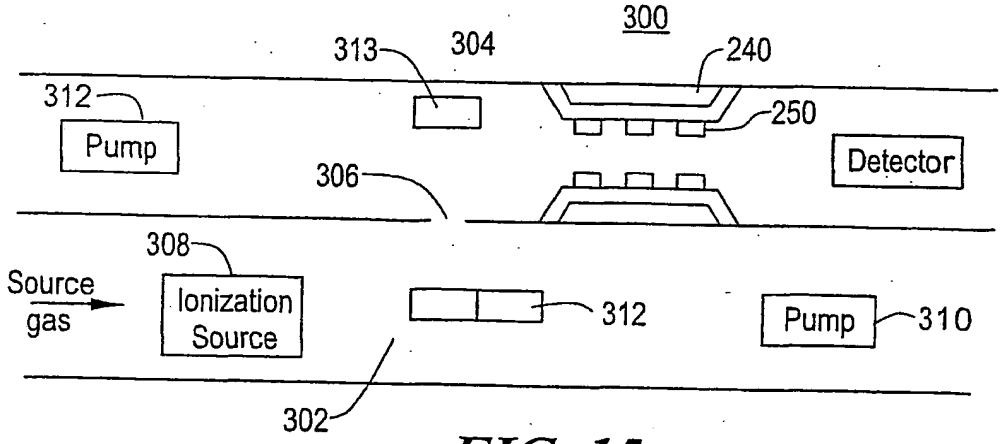

FIG. 15

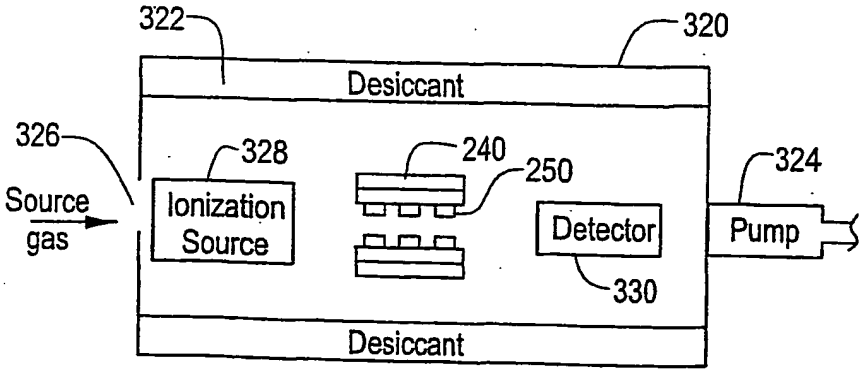

FIG. 16

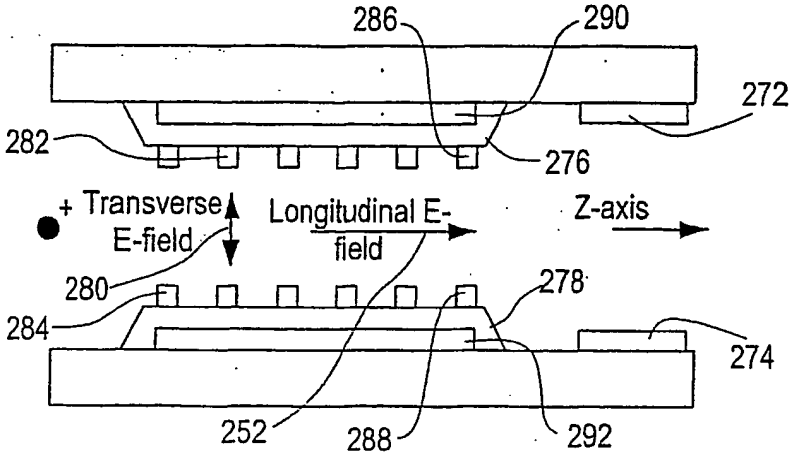
286
290
272
282
276
+ Transverse E-field
Longitudinal E-field
Z-axis
280
278
284
274
252
288
292

FIG. 17

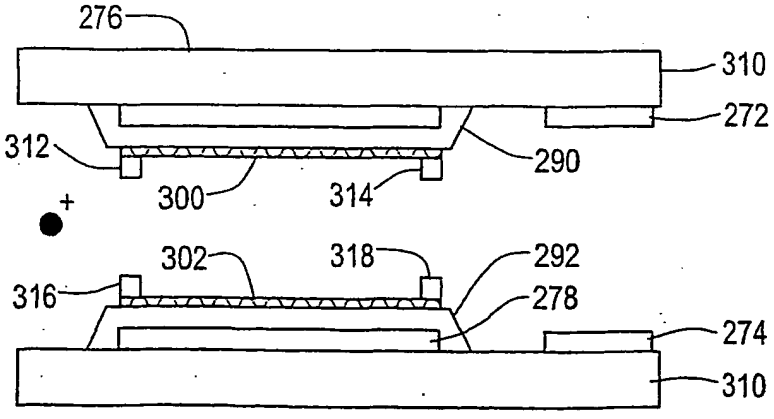
276
310
272
312
290
300
314
+
302
318
292
316
278
274
310

FIG. 18

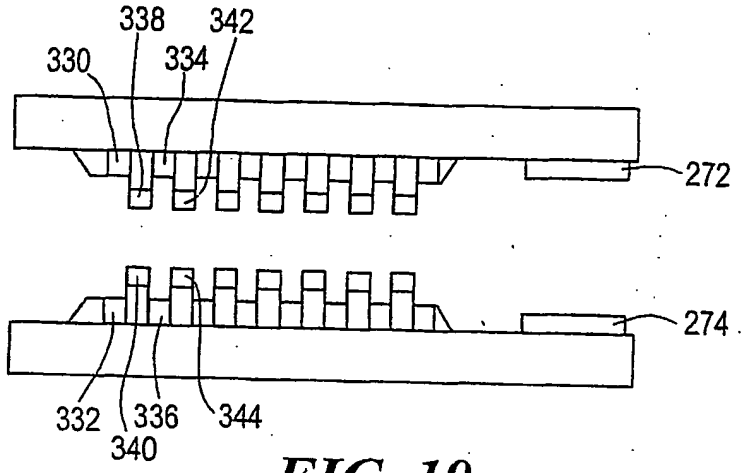

FIG. 19

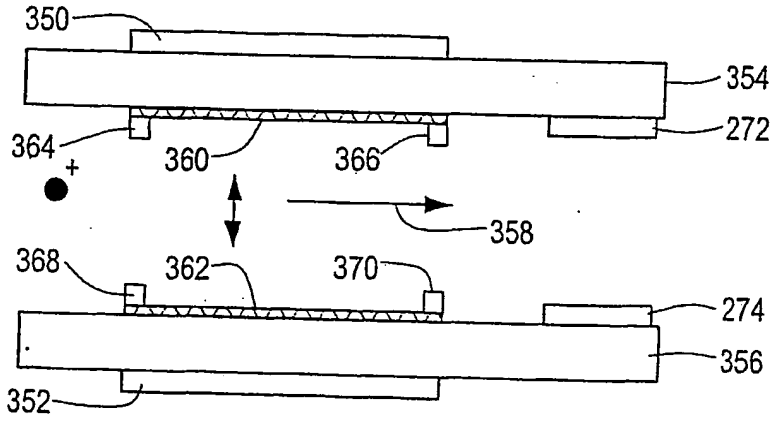

FIG. 20

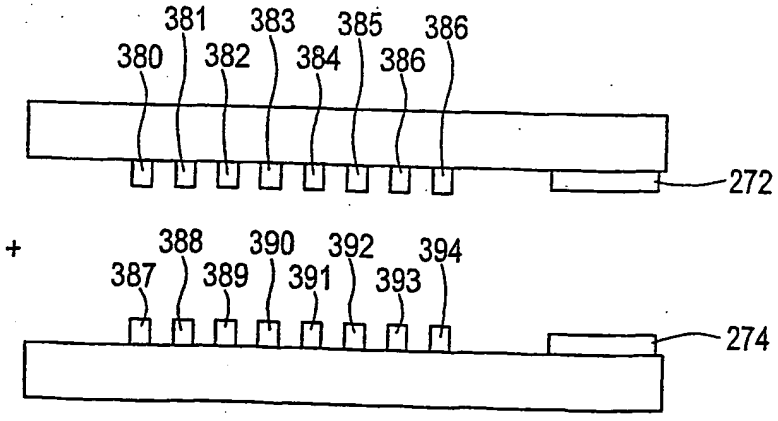

FIG. 21

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/30921

A. CLASSIFICATION OF SUBJECT MATTER
IPC(7) : H01J 49/00) :
US CL : 250/28, 287
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 250/286, 287

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WEST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,420,424 A (CARNAHAN ET. AL.) 30 MAY 1995 (30.05.95), SEE CLAIMS 1 AND 6.	1-14
A	US 5,455,417 A (SACRISTAN) 03 OCTOBER 1995 (03.10.95), SEE ENTIRE DOCUMENT.	1-14
A	US 5,789,745 A (MARTIN ET. AL.) 04 AUGUST 1998 (04.08.98), SEE ENTIRE DOCUMENT.	1-14
A	US 5,834,771 A (YOON ET. AL.) 10 NOVEMBER 1998 (10.11.98), SEE ENTIRE DOCUMENT.	1-14

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
28 FEBRUARY 2001	12 MAR 2001
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A1

(11) International Publication Number: WO 96/19822

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(21) International Application Number: PCT/GB95/02918

(22) International Filing Date: 14 December 1995 (14.12.95)

(30) Priority Data:
9425984.3 22 December 1994 (22.12.94) GB

(71) Applicant (*for all designated States except US*): THE SECRETARY OF STATE FOR DEFENCE [GB/GB]; Defence Evaluation & Research Agency, DRA Farnborough, Hampshire GU14 6TD (GB).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): LANGFORD, Marian, Lesley [GB/GB]; Intellectual Property Dept., R69 Building Defense, Evaluation & Research Agency, Farnborough, Hampshire GU14 6TD (GB). TODD, John, Francis, James [GB/GB]; University of Kent, The Chemical Laboratory, Canterbury, Kent CT2 7NH (GB).

(74) Agents: BECKHAM, Robert, William et al.; Defence Evaluation & Research Agency, Intellectual Property Dept., R69 Building, DRA Farnborough, Hampshire GU14 6TD (GB).

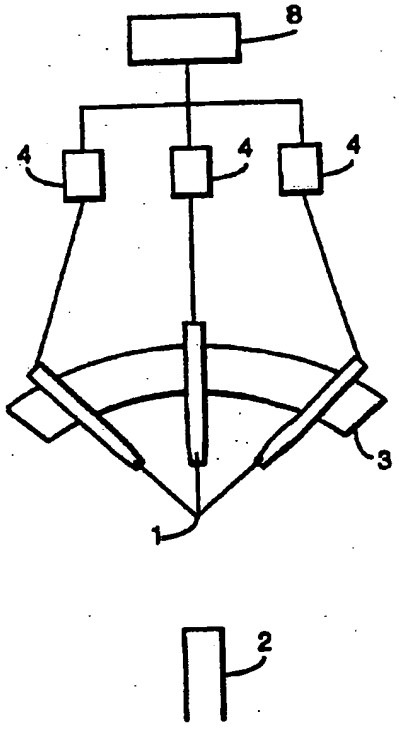
(81) Designated States: AL, AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: RADIO FREQUENCY ION SOURCE

(57) Abstract

An rf ion source suitable for low power operation over a range of pressures in air comprises discharge electrodes having one or more cathodes (1) and an anode (2). Each cathode (1) is connected to an rf signal supply (8) through an associated coupling means (4) and the anode (2) is adapted to provide a surface area over which a plasma discharge may occur that is not substantially greater than the total cathodal area over which the discharge may occur. In this way the anode (2) presents no more useful surface than is required to accommodate the optimum area of the plasma discharge thereby preventing plasma wander and enhancing the stability of the discharge over known ion sources. By configuring the electrodes such that the respective areas of the anode and the cathode(s) over which discharge occurs are separated by no more than 5 mm and by forming the electrodes to have highly curved ends and so creating a higly distorted electric field in the inter-electrode gap when the source is in operation, it is possible to create an effective discharge with very low power input even at atmospheric p ressure.



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RADIO FREQUENCY ION SOURCE

The present invention relates to a radio frequency (rf) ion source and in particular to a glow discharge source capable of low power operation over a range of pressures, including atmospheric, in air.

There exists considerable interest in the development of an ion source which is capable of operating under similar conditions to the commercially available electron impact ion source but which is more versatile and more robust than that source. The electron impact ion source is widely used in vapour analysis systems in which it is coupled to a mass spectrometer. In this source ionising particles in the form of electrons are emitted from a heated tungsten wire into a low pressure cavity, which is evacuated to pressures in the region of 10^{-4} to 10^{-3} Torr. The electrons in this cavity are accelerated by both electric and magnetic fields to an energy where impact of an electron with a sample molecule causes ionisation of that molecule. The electron impact ion source has the disadvantages that it cannot operate at high pressures and that it tends to burn out in oxygen rich environments, making the source unsuitable for use in analysis systems which operate in air at or close to atmospheric pressure.

Additionally, this source has the further disadvantage that it lacks versatility of use since it is effectively limited to the production of positively charged ions in a relatively energetic ionisation process (so called 'hard' ionisation) and usually has associated with it sample molecule fragmentation.

There also exists considerable interest in the development of an ion source capable of operating efficiently at atmospheric pressure with air as the discharge gas in which the plasma is maintained and of interfacing with commercially available mass spectrometers. This would allow for the direct sampling of air in order to monitor for the presence of impurity gases, given off for example from some drugs or explosives such as TNT, RDX and PETN.

One known device, which can operate in air at atmospheric pressure, is that described by Zhao and Lubman (Analytical Chemistry Vol 65, No 13, pages 1427-1428 and Vol 65, No 7, pages 866-876) and comprises an insulated tungsten rod driven electrode, of 0.04" diameter and ground at the end to a sharp tip which is the operative end at which a plasma discharge can occur. This electrode is coupled to an rf source and extends into a grounded 1" x 0.8"(diameter) brass cell which forms an effective "plate" electrode. In use the plasma discharge occurs between the operative end of the rod and the cell walls. The sample, ions from which are to be produced and detected, is introduced into the sample-carrying discharge gas as a liquid and carried by the gas into the brass cell where it is ionised. This device however requires a power supply capable of providing the relatively high forward power of approximately 16 Watts (W) to induce the formation and maintenance of a plasma in air at atmospheric pressure. This has the disadvantage that the power supply is relatively costly and bulky.

Furthermore, even at this relatively high forward power this ion source produces only soft (low energy) ionisation and therefore cannot substitute for the electron impact ion source. If hard (high energy) ionisation is needed then a higher power rf source would be required. This would compound the aforementioned disadvantage since to provide a hard ionising source a power supply which is capable of providing even higher forward powers than those discussed above will be necessary. Moreover, since the plasma generated by the Lubman ion source is stable only over a limited rf range of 125-375 Kilohertz (KHz) then a further disadvantage is that a relatively large ion energy distribution is likely to result which would effectively reduce the resolution of any analysis system incorporating a mass spectrometer. This is because the energy gained from the rf electric field by the ionised particles is, in part, dependent on the frequency of that rf field, as will be readily appreciated by those skilled in the art. If the ionised particles reside in the field long enough to suffer several oscillations of the rf field then their resultant energy will be close to zero, conversely if these particles are formed and ejected from the plasma within the time scale of the rf cycle then their energy will depend on the change in field potential between their formation and ejection. Thus, for a given residence time of an ion

created in a radio frequency discharge, the energy distribution of the ejected ionised particles increases as the frequency of the rf field decreases.

Generally in rf ion sources both positive ions and electrons are generated within the plasma. The difference in the mobilities of these charged particles causes a self-bias to develop on the electrode which is capacitatively coupled to the rf power supply. The degree of this self-bias is governed by the geometry of the source and in particular by the relative surface areas of the discharge electrodes, between which a plasma may form. In prior art devices the geometry of the source is such that the surface area of operative end of the driven electrode is small compared with that of the operative end of the grounded (or floating) electrode, which electrode often includes the contacting walls of the ionisation cell. This results in the generation of a negative self-bias. For this reason the driven electrode is customarily termed the "cathode" and the grounded (or floating) electrode the "anode" and therefore throughout this document the terms cathode and anode shall be taken to refer to the driven and grounded (or floating) electrodes respectively.

It is an aim of the present invention to provide a positive and negative ion producing source which is able to produce a stable plasma over a wide range of rf operating frequencies, rf peak to peak amplitudes and source pressures.

According to the present invention there is provided an rf ion source comprising one or more cathodes, an anode, and coupling means operably connected to each associated cathode for coupling the associated cathode to an rf signal supply wherein substantially the major part of the respective areas of the anode and cathode over which discharge can occur are separated by not more than 5 mm and wherein the said area of the anode over which discharge can occur is not substantially greater than the corresponding total area of the cathode or cathodes over which discharge can occur and the cathode or cathodes are configured such that, in operation of the source, the electric field in the space between the anode and the cathode(s) is substantially distorted so as to encourage maximal formation of ions and electrons therein.

By adopting a configuration for the cathode(s) and in particular a high degree of surface curvature at the end(s) thereof, the corona effect (or flow of electrons between the electrodes) is enhanced leading to a larger electron current flowing between the electrodes than would be the case in an undistorted field. As will readily be appreciated by the skilled person such effects can, for example, be achieved by using very fine electrodes for the cathode(s), typically wire electrodes. Because the density of charge on the surface of a conductor is inversely proportional to the radius of curvature at the surface of the conductor, on a negatively charged needle electrode electrons will be concentrated at the tip of the electrode and, as a consequence a greater stream of electrons will be emitted from the needle tip than would be emitted from a more blunt electrode operating at the same given applied voltage. In other words the corona effect will be enhanced. This enables the applied rf power required to produce ionisation to be reduced with respect to other geometries of cathode.

By adopting a configuration for the cathode(s) which leads to a significantly distorted electric field around the exposed edges of the cathode(s) and in the inter-electrode gap, the production of ion/electron pairs is enhanced. This is because neutral particles with a dipole moment moving in such a highly distorted electric field rapidly gain potential energy which can be converted into kinetic and/or internal energy in either case leading to an increased probability of ionisation ("field ionisation"). A further effect which has been noted by the present inventors is that useful ionisation of the surrounding gas along the exposed length of each cathode occurs with a relatively slender cathode and this provides an additional source of electrons and ions which again serves to reduce the applied power required to initiate and maintain a plasma discharge.

Moreover, the concentration of charge at the tip of a needle electrode which has been primarily designed to increase the flow of electrons between the electrodes by increasing the corona effect, is itself a further cause of distortion in the electric field in the inter-electrode gap and as a result the production of ion/electron pairs is yet further enhanced.

The overall increase in available current greatly reduces the voltages (and consequently the powers) which are required both to initiate the plasma and to maintain it. The power demands are also further minimised by establishing the inter-electrode gap at a separation of not greater than 5 mm. However, it will be readily appreciated by those skilled in the art that if the discharge electrodes are too close then the size of plasma will be too small to produce a useful ionisation. Therefore it is advantageous if each of the one or more cathodes are arranged substantially equidistant from the anode to define a gap therebetween of typically not less than 0.5 mm.

It has also been discovered that if the surface area of the anode over which plasma discharge can occur is large compared with the plasma area then the plasma can wander over the surface and that this contributes to the instability of the plasma generated in prior art sources. This is believed to be in part due to the fact that as the plasma forms it changes the surface conditions of the anode in the vicinity of the plasma so that conditions on other parts of the surface become more favourable to plasma formation. By instead configuring the anode such that the said area of the anode over which plasma discharge can occur is not substantially greater than the corresponding total area of the cathode or cathodes over which discharge can occur the ability of the plasma discharge to wander is reduced. Preferably the surface area of the anode over which plasma discharge can occur should be somewhat less than the corresponding total area of the cathode or cathodes over which discharge can occur and more specifically it is desirable that the surface area of the anode over which discharge can occur should be no greater than substantially the cross-sectional area of the discharge created when the source is operational.

It will be appreciated by those skilled in the art that the areas over which plasma discharge can occur are essentially limited to those areas respectively of the anode and cathode(s) which are in closest proximity. In a prior art ion source of the above-described type however the area of the anode which is proximal to the cathode is very extensive because substantially the whole of the ionisation chamber walls act as the anode. The increased plasma stability which is the result of configuring the

electrodes according to the present invention provides a greatly advantageous feature of the ion source according to the invention as compared to prior art sources.

Whilst it is above stated that the surface area of the anode over which discharge can occur should not be substantially greater than the corresponding total area of the cathode or cathodes over which discharge can occur and preferably not substantially greater than the cross-sectional area of the discharge itself, the minimum area which the anode may usefully have is dependent upon the thermal conductivity of the metal from which it is made ie the minimum area of the anode depends upon its ability to conduct heat away from the plasma discharge surface to prevent damage and distortion to the anode. Such area is typically not less than 0.5 times the total cathodal area over which discharge may occur.

In use the rf ion source is operated in the so called normal glow discharge regime, usually at an operating power just below that required for the onset of the so called abnormal glow discharge regime so as to ensure that the source produces the maximum area of plasma discharge under any given operating conditions. Since the power required to achieve this increases as the total surface area of the cathode(s) increases and in order to reduce the power required in operation of the source, it is advantageous to make the cathodal area (and consequently the anode) as small as possible whilst still being capable of providing a useful plasma discharge. For this reason and also bearing in mind the requirement for severe distortion of the electric field in the inter-electrode gap, it will be apparent that all of the discharge electrodes for the source of this invention may conveniently be formed using commercially available wire, thin rod or bar. Such materials also have the advantage of being inexpensive both as regards initial cost and as regards manufacture into suitable electrodes.

Although the ion source of this invention may be operated at a wide range of rf frequencies, particularly up to the MHz region, the use of high rf frequencies is particularly advantageous since, from the foregoing discussion on frequency effects, it is clear that as the rf frequency increases the energy distribution of the ionised particles

decreases thereby increasing the resolution of an analysis system which incorporates a mass spectrometer operatively coupled to the source of the present invention.

Most usefully, the applied rf power required to produce ionisation may be further reduced by having the coupling means adapted to capacitively couple its associated cathode through an rf power amplifier to the rf source since in this arrangement the flow of any net current through the system is substantially reduced thereby allowing the voltage drop between the each of cathodes and the anode to increase.

The reductions in rf power required to form and maintain a plasma enables the source to be operated at rf powers typically in the region of as low as only 0.1 W for air as the sample carrying discharge gas when operated at 1 Torr and in the region of 1 W when operated at atmospheric pressure. This relatively low power requirement has an advantage that it is possible to power even a multi-cathode source, operating at atmospheric pressure, using miniaturised components on a circuit board which facilitates their large volume production. Furthermore, since the source is able to operate at such low powers then where hard ionisation is required, for example when the source is used to substitute for the electron impact source, the additional power requirements may still be met using miniaturised components. Most preferably each coupling means comprises a variable capacitance matching circuit in operable connection with an individual variable power rf amplifier. In this configuration the forward power at each cathode may be individually maximised and the magnitude of the rf voltage amplification individually adjusted for each plasma discharge gas.

Additionally, when a multiple cathode arrangement is used preferential plasma formation may occur between the anode and the cathode where the characteristics were energetically most favourable, for example the closest cathode if the anode/cathode separation is not identical for each cathode. This results in the problem that plasma discharges at the other cathode or cathodes would only be achieved by a significant increase in the amplification of the rf power. This problem may be alleviated if each cathode has its own variable power rf amplifier and matching circuit.

Also usefully the separation between the anode and the one or more cathodes is variable so as to permit optimisation of the plasma discharge. Usefully, where more than one cathode is employed then the rf signal supply may comprise a plurality of rf signal generators, one for each cathode. This has the advantage that the phase of each rf signal to each cathode could be altered. In an especially preferred embodiment the ion source according to the present invention comprises a single cathode and anode arrangement. This has the advantages of ease of manufacture and operation compared with the multiple cathode source.

It has been found that with the ion source of the present invention a range of operating conditions in relation to the pressure and flow rate of the sample carrying discharge gases may be employed without unduly reducing the stability of the plasma discharge. By contrast a direct current glow discharge ion source can only operate in a stable fashion within a narrow range of pressures around 1 Torr.

In order to protect the discharge electrodes against physical damage and in order to facilitate the introduction of samples to be ionised, especially in gases other than air or where the pressure of the gas is required to be either above or below atmospheric pressure to optimise ionisation conditions, the ion source of the present invention may usefully further comprise an ionisation chamber adapted to provide for the through flow of sample carrying gas and in which the discharge electrodes are located. This chamber may be configured to have an inlet and an outlet to provide for the through flow of the sample carrying gas and an interface orifice through which samples of ionised particles can pass. In this configuration the discharge electrodes may be positioned within the ionisation chamber so as to be capable of providing a plasma discharge proximal to and across both the inlet and the outlet.

Charged particles which leave the rf plasma axially, ie in the direction of one of the discharge electrodes, gain variable amounts of energy in the accelerating potential field associated with the cathode or the anode. This gives rise to a broad energy distribution of these particles. Thus, in situations where it is important to minimise the

energy distribution of the ionised particle samples, for example where the samples are to be analysed by a mass spectrometer, it is preferable to arrange the interface orifice and the discharge electrodes so that only ionised particles leaving the plasma at an angle, and preferably substantially perpendicular, to the axis of the plasma connecting the discharge electrodes pass through the orifice. Using this arrangement the ionised particles do not pass through the high field regions near the electrodes.

A means for accelerating the flow rate of the sample carrying gas, for example a pump or fan, may usefully be incorporated into one or both of the inlet or the outlet thereby effectively increasing the availability of the sample for ionisation. It will be appreciated by those skilled in the art that the actual flow rate will be dependent to some extent on the use to which the ion source will be put, for example where a narrow energy distribution is required then the time the ions are resident within the plasma should be longer and consequently the flow rate slower than when there is not this requirement, but flow rates of typically 6 cm^3/s may be used when sampling substances in air.

Embodiments of the rf ion source according to the present invention will now be described, by way of example only, with reference to the drawings in the accompanying figures of which:

Figure 1 is a schematic representation of a 3-cathode configuration of the ion source according to the present invention.

Figure 2 is a schematic representation of a coupling means suitable for use in an ion source according to the present invention.

Figure 3 is a schematic representation of a single cathode configuration in place within an ionisation chamber.

Figure 4 is a schematic representation of the embodiment of figure 3 interfaced with a commercially available ion trap mass spectrometer.

Figure 5 shows representative spectra obtained for water clusters using the configuration shown in Figure 4 operating in air at 960 mTorr where a) is collected at 2.1 MHz and b) is collected at 1.6 MHz.

Figure 6 shows representative spectra obtained for FC-43 using the configuration shown in Figure 4 operating in air at 960 mTorr with an rf frequency of 2 MHz where a) is using 0.1 W of applied power and b) is using 0.4 W of applied rf power.

Figure 7 shows representative negative-ion mass spectra produced by generating a radio frequency discharge in air at 800 mTorr with an rf frequency of about 2 MHz and selecting negative ions from the discharge. (a) shows the spectrum up to m/z 450, (b) details lower mass ions and (c) details some higher mass ions.

The rf ion source shown in Figures 1 and 2 comprises three cathodes (1) arranged to be equi-distant at a spacing of 2 mm from the single anode (2). These discharge electrodes (1,2) are fabricated from 0.9mm diameter Fecralloy wire (commercially available from Goodfellow Cambridge Limited, Cambridge Science Park, Cambridge UK, [product code: FE085240]), but it will be appreciated that any suitably dimensioned electrical conductor may be substituted, with the tip of the cathode (1) being drawn into a needle point.

The cathodes (1) are electrically insulated from each other by mounting them in an insulating block (3) which is positioned on the cathodes (1) so as not to be susceptible to damage from the heat of the plasma discharge. A separate coupling means (4) is provided for each cathode (1) comprising a linear response rf amplifier (5) which is coupled to its respective cathode (1) through a wattmeter (6) and associated variable capacitance matching circuit (7). The variable capacitance matching circuit (7) is configured so that the cathode (1) can be connected to the electric circuit at (C) and rf signal supply (8) can be connected to the electric circuit before the amplifier (5) at point (S). Thus the coupling means is essentially similar to ones used in prior art ion source except that the rf amplifier is adapted to operate in the sub-W amplification

region. Each low powered linear response rf amplifier (5) is operably connected to an rf signal supply (8). It will be appreciated by those skilled in the art that the rf signal supply (8) may comprise a common rf signal generator or may comprise three such generators, one connected to each cathode, depending on the application to which the source is to be put.

Referring now to Figure 3, the ion source comprises a single, flat ended cathode (31) and an anode (32) which again are formed from 0.9 mm diameter Fecralloy wire or some other suitably dimensioned electrical conductor. These discharge electrodes (31,32) are positioned so that a plasma discharge will occur across and approximately 0.5 cm from a 200 μm diameter inlet (10) for a sample carrying gas through a wall of the ionisation chamber (9). The cathode (31) and the anode (32) are each maintained in this position by an insulating ceramic bridge support (33) with the cathode (31) passing through and insulated from the ionisation chamber (9) to connect with an rf signal supply (8). This comprises a single rf signal generator and is connected to the cathode via a coupling means (4) whereas the anode (32) is connected to earth through the walls of the ionisation chamber (9). The ionisation chamber (9) is further provided with an outlet (12) through which the gas is drawn out by a pump (13). An interface orifice (14) is also provided in a wall of the ionisation chamber (9), opposite the inlet (10) and positioned so as to be capable of collecting only samples of ions emitted substantially perpendicular to the axis (A) of the plasma which connects the discharge electrodes (31,32).

An example of the application for which the ion source of Figure 3 is particularly suitable is shown schematically in Figure 4. Here the ionisation chamber (9) is arranged so that the interface orifice (14) is operably connected to an electrostatic lensing system (15) and then to a conventional mass spectrometer (16), such as the ion trap mass spectrometer commercially available from Finnigan MAT Limited, Paradise, Hemel Hempstead, Herts, UK. This arrangement is particularly suited to the continuous sampling and analysing of the atmosphere to identify trace amounts of impurities contained therein because the ion source according to the

present invention is capable of low power operation in air over a range of pressures, including atmospheric pressure.

Examples of mass spectra plots of ion intensity against atomic mass to atomic charge ratio (m/z) which were obtained using an arrangement similar to that shown in Figure 4 are provided in Figures 5 to 7. These spectra were generated using a plasma discharge generated in air below atmospheric pressure with applied rf powers of the order of 0.1 to 0.5 W and contain peaks characteristic both of the air and of the impurity (Figures 5 and 6). The impurity deliberately introduced into the air is either water clusters or small quantities of FC-43 (perfluorotri-n-butylamine, $C_{12}F_{27}N$) vapour and is introduced by allowing the air stream to pass over a glass spoon containing typically 0.1 ml of water or FC-43 liquid before it passed through the inlet (10). No impurity was introduced in the case of the spectra provided in Figure 7.

Figures 5 a and b show mass spectra for water cluster impurities collected using a) 2.1 MHz rf field and b) 1.6 MHz rf field, both at a power of 0.1 W and at a pressure of 960 Torr. Water clusters, $H_3O^+(H_2O)_n$, require little energy to dissociate them and therefore are a useful indicator of the ability of the plasma discharge to cause fragmentation or ionisation. The peaks associated with different values of n are indicated on Figures 5 (a) and (b). In the spectrum generated at 2.1 MHz clusters were recorded with n=1-9 whereas when the rf frequency was reduced to 1.6 MHz clusters with n>3 were lost. The greater fragmentation at the lower frequency indicates that the ionising particles from the ion source become harder as the rf frequency is decreased.

Figures 6 a and b show representative mass spectra of ions produced from FC-43 and the variations in their intensity with applied rf power. Figures 6 a and b show mass spectra obtained using a) 0.1W and b) 0.4W and indicate the presence of positive ions identified as CF_3 (m/z=69), C_3F_5 (m/z=131) and $C_5F_{10}N$ (m/z=264). These spectra illustrate that effective ionisation occurs even at these low powers and that, analogous with the high powered prior art ion source, ionisation becomes harder as the power increases.

Figure 7 demonstrates the operation of the rf ion source in negative-ion collection mode. These spectra were collected at a source pressure of 800mTorr and were generated by an rf discharge created in air, without the deliberate introduction of any impurity into the air stream.

CLAIMS

1. An rf ion source comprising one or more cathodes, an anode, and coupling means operably connected to each associated cathode for coupling the associated cathode to an rf signal supply wherein substantially the major part of the respective areas of the anode and cathode over which discharge can occur are separated by not more than 5 mm and wherein the said area of the anode over which discharge can occur is not substantially greater than the corresponding total area of the cathode or cathodes over which discharge can occur and the cathode or cathodes are configured such that, in operation of the source, the electric field in the space between the anode and the cathode(s) is substantially distorted so as to encourage maximal formation of ions and electrons therein.

2. An rf ion source as claimed in Claim 1 wherein the surface area of the anode over which the discharge can occur is less than the corresponding total area of the cathode or cathodes over which discharge can occur.

3. An rf ion source as claimed in claim 2 wherein the surface area of the anode over which discharge can occur is no greater than substantially the cross-sectional area of the discharge created when the source is operational.

4. An rf ion source as claimed in any preceding claim wherein the anode and cathode(s) are fabricated from wire.

5. An rf ion source as claimed in any preceding claim wherein each of the one or more cathodes is formed into a needle point.

6. An rf ion source as claimed in any preceding claim wherein each of the one or more cathodes are arranged substantially equi-distant from the anode to define a gap between the anode and each cathode of from 0.5mm to 5mm.

7. An rf ion source as claimed in Claim 6 wherein the each of the one or more cathodes and the anode are moveable relative to one another to define a variable gap therebetween.

8. An rf ion source as claimed in any of the preceding claims wherein the coupling means is adapted to capacitively couple its associated cathode to an rf signal supply.

9. An rf ion source as claimed in Claim 8 wherein the coupling means comprises a variable capacitance matching circuit in operable connection with an rf power amplifier.

10. An rf ion source as claimed in Claim 9 wherein the rf power amplifier is a low power linear response amplifier.

11. An rf ion source as claimed in any preceding claim wherein the number of cathodes is one.

12. An rf ion source as claimed in any of the preceding claims further comprising an ionisation chamber in which the discharge electrodes are housed, said chamber having an inlet and an outlet configured to provide for the through flow of sample carrying gas and an interface orifice adapted to permit the passage of ionised particles out of the ionisation chamber.

13. An rf ion source as claimed in Claim 12 wherein the discharge electrodes are cooperatively configured with the interface orifice so that only those ions emitted at an angle to an axis through the plasma and the discharge electrodes are capable of passing through the interface orifice.

14. An rf ion source as claimed in Claim 13 wherein the cooperative configuration is such that only those ions emitted substantially perpendicular to the axis are capable of passing through the interface orifice.

15. An rf ion source as claimed in any of the claims 12, 13 or 14 wherein the discharge electrodes are positioned within the ionisation chamber so as to be capable of providing a plasma discharge proximal to and across the inlet.

16. An rf ion source substantially as hereinbefore described with reference to Figures 1 to 3 of the accompanying drawings.

Fig.1.

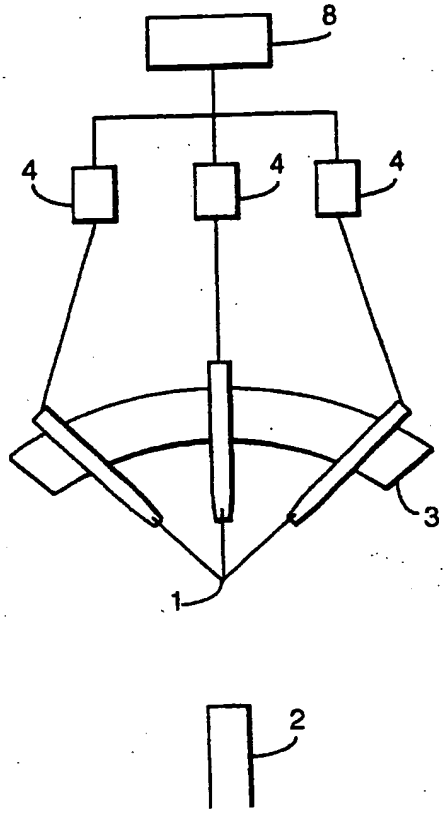

Fig.2.

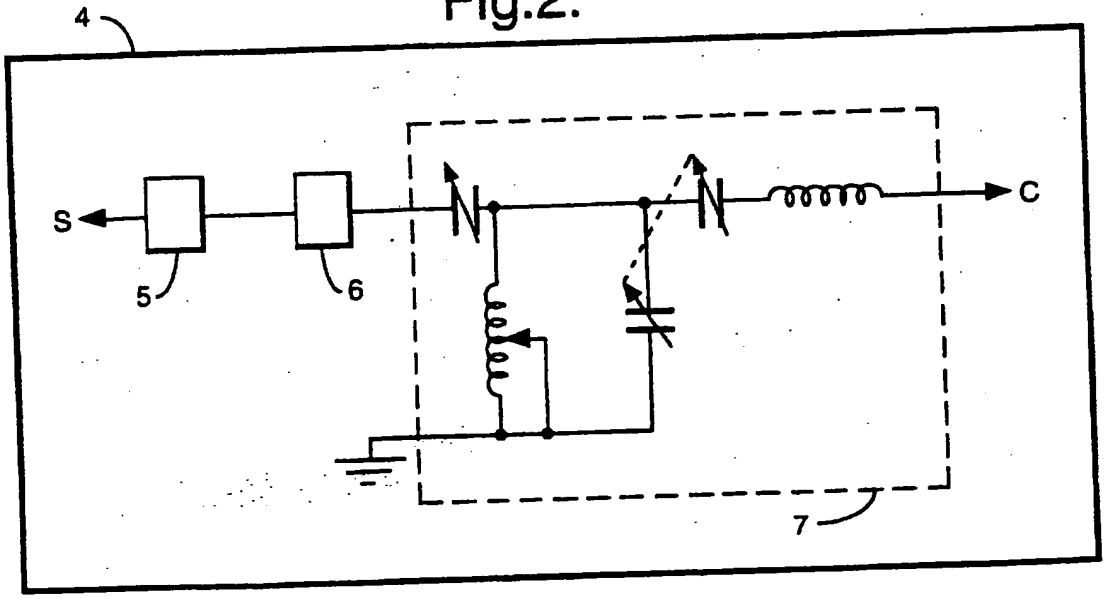

Fig.3.

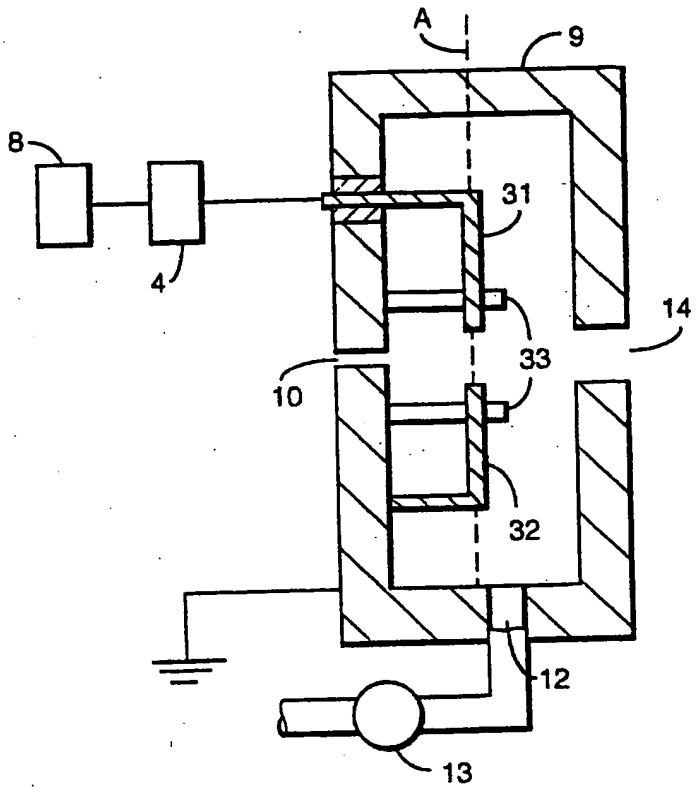

Fig.4.

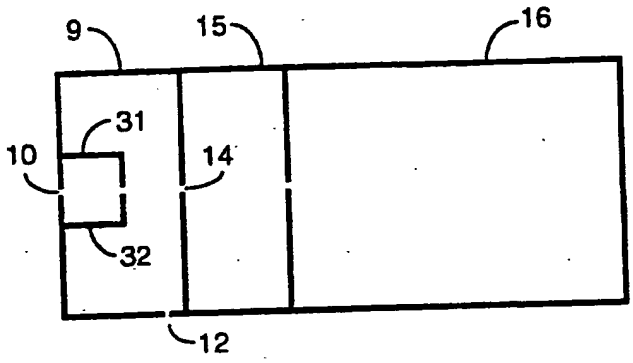

Fig.5.

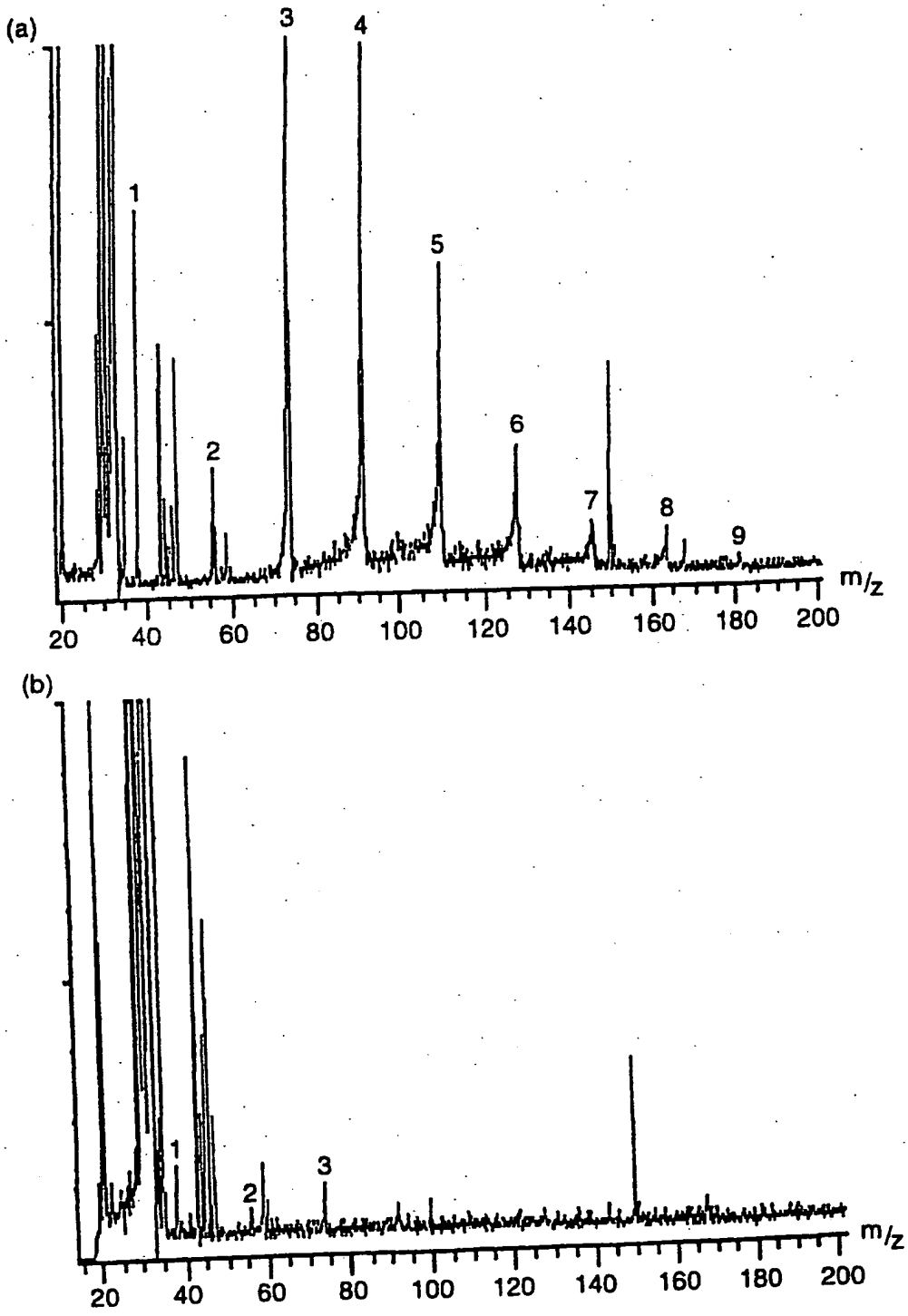
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Fig.6.

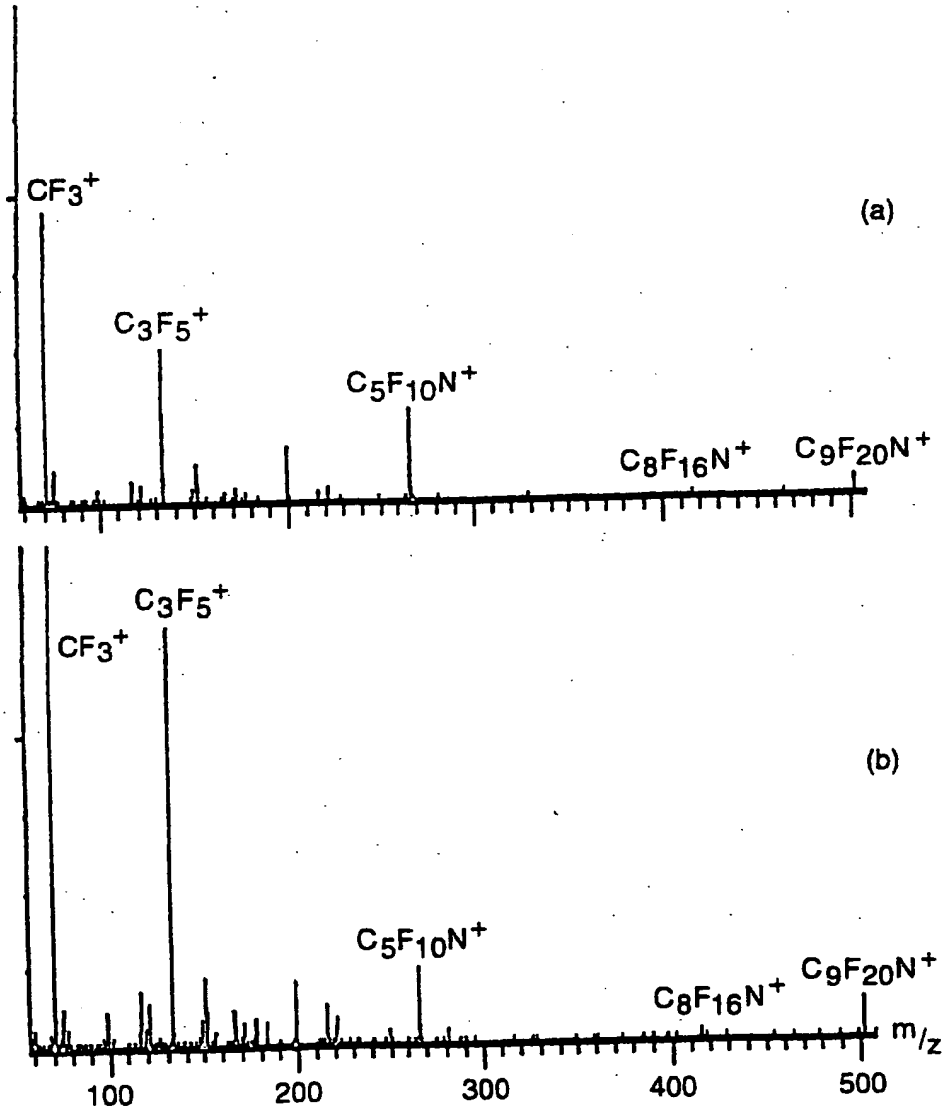
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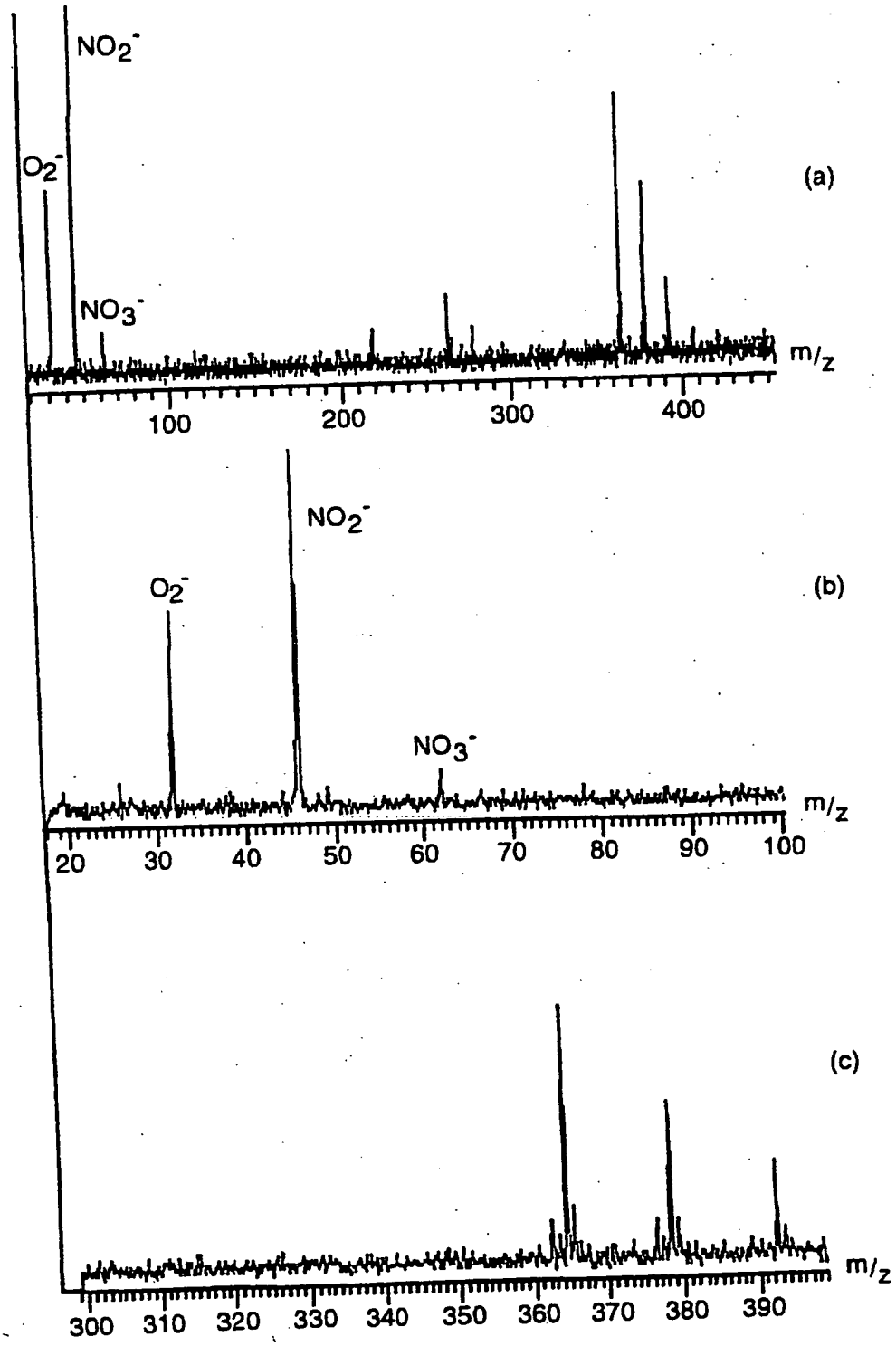
Fig.7.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INTERNATIONAL SEARCH REPORT

PCT/GB 95/02918

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01J49/10 H01J27/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	INSTRUMENTS AND EXPERIMENTAL TECHNIQUES, vol. 26, no. 5, 1983 NEW YORK US, pages 1188-1190, M S ABDUGABBAROV ET AL. 'IOn-source attachment to the MI-1201 mass spectrometer for analysing secondary ions' see the whole document ---	1-5, 11-14,16
Y	ANALYTICAL CHEMISTRY, vol. 64, no. 13, 1 July 1992 pages 1426-1433, XP 000295869 JIANGUO ZHAO ET AL 'LIQUID SAMPLE INJECTION USING AN ATMOSPHERIC PRESSURE DIRECT CURRENT GLOW DISCHARGE IONIZATION SOURCE' cited in the application see page 1427, right column - page 1428, left column ---	1-5, 11-14,16

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents:

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 March 1996	22.03.96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Colvin, G

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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2

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